

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2004-152925

(43)Date of publication of application : 27.05.2004

(51)Int.Cl.

H01L 21/304

C11D 7/26

C11D 7/32

C11D 7/36

C11D 17/00

C23G 1/00

(21)Application number : 2002-315359

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(22)Date of filing : 30.10.2002

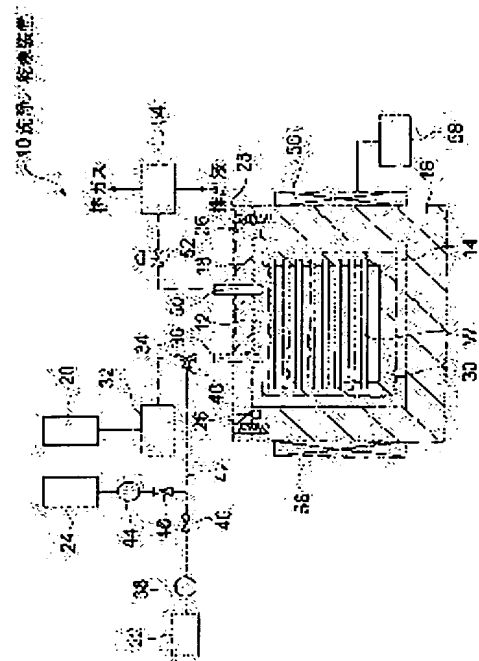
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(54) WASHING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a washing method wherein a body to be washed, which is contaminated by a metal, is washed and cleaned without providing any damage to the body to be washed.

SOLUTION: A cassette 30 for retaining the body to be washed is stored into a processing chamber 14 which is sealed thereafter, then, a supercritical carbon dioxide is introduced from a supplying source 20 into the processing chamber. Subsequently, a three-way valve 34 is adjusted to add a cleaning coagent, such as citric acid or the like, to the carbon dioxide with a predetermined adding rate through a supplying port 48. In this case, temperature in the processing chamber is controlled by a temperature control device 58 and an exhaust pressure valve 52 is opened when a pressure in the chamber becomes higher than a given value to discharge the carbon dioxide and the cleaning coagent via a discharging liquid separating device 54. The body to be washed is dipped into the carbon dioxide for a predetermined period of time to remove the heavy metallic contaminant and, thereafter, the supply of the washing coagent is stopped while dipping the body to be washed into the carbon dioxide as it is and only the carbon dioxide is supplied into the processing chamber as a rinse solution to discharge the washing coagent while thinning gradually the concentration of the washing coagent. Finally, the processing chamber is evacuated to discharge the carbon dioxide.



LEGAL STATUS

[Date of request for examination]

27.07.2005

[Date of sending the examiner's decision of rejection]

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[Kind of final disposal of application other than
the examiner's decision of rejection or
application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of
rejection]

[Date of requesting appeal against examiner's
decision of rejection]

[Date of extinction of right]

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[JP,2004-152925,A]

CLAIMS

[Claim(s)]

[Claim 1]

In the approach of washing the washed body by which metal contamination is carried out by supercritical fluid,

The washing approach characterized by having the washing process which the supercritical fluid which added the organic acid or the chelating agent with the predetermined appending rate as a washing assistant is used as a penetrant remover, and the washed body is contacted to the supercritical fluid which added the washing assistant, and is washed.

[Claim 2]

The washing approach according to claim 1 characterized by having the process which gasifies supercritical fluid and dries the washed body following a washing process.

[Claim 3]

The rinse process which supplies only supercritical fluid and performs rinse washing to the washed body following a washing process,

Subsequently, the process which supercritical fluid is gasified [process] and dries the washed body

The washing approach according to claim 1 characterized by ****(ing).

[Claim 4]

In the approach of washing the washed body by which metal contamination is carried out by supercritical fluid,

The process which uses 1 tub type washing / dryer which has washing/desiccation chamber of one tub, adds and supplies an organic acid or a chelating agent to supercritical fluid with a predetermined appending rate as a washing assistant at washing/desiccation chamber which holds the washed body, and washes the washed body,

Subsequently, the process which carries out rinse washing of the washed body, permuting the supercritical fluid which supplied only supercritical fluid to washing/desiccation chamber, and added the washing assistant by supercritical fluid, Subsequently, the process which supercritical fluid is gasified and removed [process] and dries the washed body

The washing approach characterized by ****(ing) and performing washing processing and desiccation processing one by one within washing/desiccation chamber of one tub.

[Claim 5]

The washing approach given in any 1 term of claims 1-4 characterized by using a supercritical carbon dioxide as supercritical fluid.

[Claim 6]

The washing approach according to claim 5 characterized by dissolving a polar organic solvent in a supercritical carbon dioxide, and subsequently to a supercritical carbon dioxide pouring in a washing assistant solution.

[Claim 7]

The washing approach given in any 1 term of the claims 1-6 characterized by using a citric acid or a malic acid as an organic acid.

[Claim 8]

The washing approach given in any 1 term of the claims 1-7 characterized by using a diethylenetriamine pentaacetic acid (DTPA), triethanolamine (TEA), 1, 2-cyclohexane diamino tetraacetic acid (CDTA), a diethylene triamino 5 methylene phosphoric acid (DTPMP) and 1, 1, 1, 5 and 5, the 5-6 fluoride -2, or 4-2,4-pentanedione as a chelating agent.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

This invention relates to the optimal washing approach for washing of the wafer which was formed with the application of the washed body polluted with metals, such as a tungsten, aluminum, and copper, especially CMP, or ECP and which embeds and has wiring in more detail about the washing approach.

[0002]

[Description of the Prior Art]

At the process which forms metal wiring of semiconductor devices, such as a transistor, after forming the metal membrane for metal wiring formation conventionally, on a

metal membrane, the resist film is formed, patterning of the resist film is carried out, and an etching mask is formed. Then, a metal membrane is etched by the dry etching method from on an etching mask, and metal wiring is formed.

Moreover, at the process which forms the metal plug which connects vertical wiring with the wiring structure of a semiconductor device, after forming the metal membrane for metal plug formation and embedding a contact hole on the insulator layer in which the contact hole was formed, etchback of the whole metal membrane surface is carried out, and the metal plug is formed.

[0003]

By the way, in case the metal membrane on an insulator layer is ground and removed henceforth [a 0.18 micron device generation] on the occasion of formation of embedding metal wiring and a metal plug as high integration of a device, high aspect-ization, etc. progress in recent years, they are chemical mechanical polishing (ChemicalMechanical Polishing : CMP) and electrolytic polishing (Electro Chemical Polishing).

: It is coming to apply ECP.

[0004]

For example, in wiring formation of a semiconductor device, the so-called DAMASHIN process which grinds the metal layer on an insulator layer, removes by CMP or ECP, embeds, and forms metal wiring is used.

a DAMASHIN process — first — reactive ion etching (RIE) — law etc. — SiO₂ on a wafer etc. — a layer insulation layer is etched and a wiring gutter is formed. Subsequently, metal membranes, such as aluminum film and a copper film, are formed by the CVD method, or a spatter or the galvanizing method all over a wafer, for example, a wiring gutter is embedded, CMP and ECP grind and remove the metal membrane on a layer insulation layer continuously, it embeds at wiring Mizouchi, and metal wiring is formed.

[0005]

Moreover, similarly formation of a metal plug has applied CMP. first, SiO₂ etc. — a layer insulation layer — reactive ion etching (RIE) — a connection hole is formed by law etc. Subsequently, for example, the titanium film, the titanium nitride film, the tantalum nitride film, etc. are formed all over a wafer including the porous wall of a connection hole as an adhesion layer with a spatter or a CVD method, for example, the tungsten film is continuously formed on an adhesion layer with a CVD method, and a connection hole is embedded. Subsequently, by CMP, the tungsten film and adhesion layer on a layer insulation layer are ground, and a metal plug is formed in a connection hole.

[0006]

By the way, by the CMP method of the conventional metal membrane, since the polished surface of a metal membrane was washed after laying the wafer on the rotating polish plate (it is also called a platen) and grinding the metal membrane on a wafer using a slurry-like abrasive material, there were the following problems.

I hear that it is easy to generate a blemish (scratch) on that a lot of particle set to the 1st from the metallic oxide originating in an abrasive material slurry, a ceramic, etc. remains on a wafer front face, and a wafer front face, and it is shown in them.

It is concern that metal contamination of the wafer front face is carried out with the metallic oxide contained in an abrasive material slurry the 2nd. If heavy metal contamination occurs on an interlayer insulation film or in an interlayer insulation film especially, since leak between wiring will be caused, it becomes a very serious problem. Also when the metal membrane on an interlayer insulation film is ground by ECP, the same heavy metal contamination poses a problem.

[0007]

On the other hand, for improvement in the speed of LSI, it is indispensable to reduce the capacity between wiring. Then, in order to reduce the capacity between wiring, the low dielectric constant film is used as an interlayer insulation film during wiring.

Furthermore, in order to form the interlayer insulation film of much more a low dielectric constant, the attempt which makes porosity membraneous quality of not only selection of a film ingredient but an interlayer insulation film has accomplished.

[0008]

Here, how to use the porosity low dielectric constant film as an interlayer insulation film, embed according to a single DAMASHIN process with reference to drawing 5 , and form metal wiring and a metal plug is explained. It is a sectional view explaining each process at the time of the porosity low dielectric constant film being used for (c) from drawing 5 (a), and forming metal wiring and a metal plug according to a single DAMASHIN process.

First, as shown in drawing 5 (a), through the etching mask layer 78, the porosity low dielectric constant film 80 is formed on the substrate film 76, and the contact hole 82 and wiring gutter 84 which are arrived at subsequently to the substrate film 76 at the low dielectric constant film 80 are formed.

Subsequently, as shown in drawing 5 (b), the metal membrane 88 for metal plug formation is continuously formed the reaction prevention layer 86 and formed in the wall of a contact hole 82 and a wiring gutter 84 on the low dielectric constant film 80, and a contact hole 82 and a wiring gutter 84 are embedded.

Subsequently, as shown in drawing 5 (c), while giving CMP, grinding a metal membrane 88 and exposing the low dielectric constant film 80, the metal plug 90 and the embedding wiring 92 are formed.

[0009]

By the way, as shown after CMP at drawing 5 (c), the heavy-metal-contamination object 93 produced from the abrasive material slurry of metal membrane residue or CMP is generated on the low dielectric constant film 80 or in the low dielectric constant film 80. If it produces commercially while metal contamination of the low dielectric constant film 80 had been carried out with these heavy-metal-contamination objects 93, since leak between wiring etc. will occur, it is required to remove the heavy-metal-contamination object 93 and to defecate the low dielectric constant film 80.

[0010]

Moreover, in case it embeds according to a dual DAMASHIN process and wiring is formed, as shown in drawing 6 (a), the 1st porosity low dielectric constant film 96, the 1st etching mask layer 98, the 2nd porosity low dielectric constant film 100, and the 2nd etching mask layer 102 are formed one by one on the substrate film 94. Then, the contact hole 104 which reaches the substrate film 94, a contact hole 106, and a wiring gutter 108 are formed using the etching mask formed from the 1st etching mask layer 98 and the 2nd etching mask layer 102. Subsequently, the reaction prevention layer 110 is formed in the wall of contact holes 104 and 106 and a wiring gutter 108.

As shown in drawing 6 (b), the metal membrane 112 for wiring and metal plug formation is formed on the 2nd etching mask layer 102, and contact holes 104 and 106 and a wiring gutter 108 are embedded.

Subsequently, as shown in drawing 6 (c), while giving and grinding CMP in a metal membrane 112 and the 2nd etching mask layer 102 and exposing the 2nd porosity low dielectric constant film 100, the metal plugs 114 and 116 and the embedding wiring 118 are formed.

[0011]

By the way, as shown after CMP at drawing 6 (c), the heavy-metal-contamination object 120 produced from metal membrane residue or an abrasive material slurry is generated on the 2nd porosity low dielectric constant film 100 or in the film.

If it produces commercially while metal contamination had been carried out with these heavy-metal-contamination objects, since leak between wiring etc. will occur, it is required to remove a heavy-metal-contamination object and to defecate the 2nd porosity low dielectric constant film 100.

In addition, it is a sectional view explaining each process at the time of the porosity low

dielectric constant film being used for (c) from drawing 6 (a), respectively, and forming metal wiring and a metal plug according to a dual DAMASHIN process.

[0012]

Although these heavy-metal-contamination object had to be removed in order to manufacture LSI devices which are not produced, such as leak between wiring, as stated above, there were the following problems which should be solved on that occasion.

Usually, in removing heavy metal, wet washing using water is performed as wash water, and, subsequently it is dry. However, since the differential pressure of the pressure of a penetrant remover and atmospheric pressure occurs in a gas-liquid interface when penetrant removers, such as water with large surface tension, frequent the hole of the porosity low dielectric constant film on the occasion of washing, the hole of the porosity low dielectric constant film is crushed, membraneous quality changes, and the dielectric constant of the low dielectric constant film becomes high in many cases. Now, the effectiveness which uses the porosity low dielectric constant film declines.

[0013]

What is necessary is to use a fluid with small surface tension and just to do washing/desiccation of, in order to make it a hole not crushed. For example, although the surface tension of water is about 72 dyn/cm, since the surface tension of a methanol is about 23 dyn/cm, after carrying out backwashing by water rather than it makes it dry immediately after carrying out backwashing by water, a methanol permutes water and the direction subsequently dried tends to suppress change of the membraneous quality of the low dielectric constant film.

However, since it is not so small as the surface tension of a methanol can also be disregarded, a hole is crushed to some extent. Therefore, change of membraneous quality cannot be prevented completely and it does not become a perfect problem solving.

[0014]

It is drying after it makes it dry after washing using the fluid whose surface tension is zero as a rinse or carrying out a rinse with such a liquid, in order to make it the hole of the porosity low dielectric constant film not crushed, or surface tension permutes a rinse by the fluid of zero.

Surface tension can mention supercritical fluid as a fluid of zero. A supercritical condition is one of the condition phases which the matter takes under the critical temperature of a proper, and the critical pressure to the matter, and supercritical fluid means the fluid in a supercritical condition.

While the solvent power of supercritical fluid over other liquids and solid-states is

almost equivalent to the fluid of a liquid condition, the viscosity is remarkably small and it has the unique property in which a diffusion coefficient is very large. If it puts in another way, it can be said to be a liquid with a gaseous property.

Therefore, since supercritical fluid does not form a gas-liquid interface, surface tension becomes zero. Then, if the washed body is dried in the state of supercritical, since surface tension does not exist, the differential pressure by generating of a gas-liquid interface will be produced at all.

[0015]

Since supercritical fluid will be promptly gasified if a pressure turns into below the critical pressure, after washing using supercritical fluid, supercritical fluid can be easily emitted by decompressing.

Therefore, after the porosity low dielectric constant film washes the substrate exposed to a front face, After washing by the penetrant remover directly from a penetrant remover and carrying out a rinse by the rinse subsequently Or after carrying out a rinse and another liquid permutes a rinse, the liquid adhering to a substrate is easily removable by contacting the substrate to which the penetrant remover, the rinse, or another liquid has adhered to the supercritical fluid in a proof-pressure container, and dissolving these liquids in supercritical fluid.

Subsequently, a substrate can be picked out from a proof-pressure container in atmospheric air by reducing the pressure in a proof-pressure container below to the critical pressure, maintaining the temperature in a proof-pressure container more than critical temperature, and gasifying supercritical fluid.

Since the surface tension of supercritical fluid is very small, in case supercritical fluid is removed from a substrate front face, the stress given to the microstructure of a wafer, for example, the hole of a pattern or the porosity low dielectric constant film, with the surface tension is extent which can be disregarded. As [arise / therefore, / on the porosity low dielectric constant film / deterioration] (JP,2000-154273,A)

[0016]

Many matter with which it is checked as supercritical fluid that it will be in supercritical conditions, such as a carbon dioxide, ammonia, water, alcohols, aliphatic saturated hydrocarbon of low molecular weight, benzene, and diethylether, can be used.

In these matter, without putting that handling is easy and the washed body to an elevated temperature, washing / since it says that it can dry, the carbon dioxide with the supercritical temperature near 31.3 degrees C and a room temperature is one of the matter desirable as a penetrant remover.

[0017]

[Patent reference 1]

JP,10-135170,A (drawing 1)

[Patent reference 2]

The patent No. 2574781 official report (drawing 1)

[0018]

[Problem(s) to be Solved by the Invention]

However, there were the following problems in the conventional washing approach by the supercritical carbon dioxide.

Since the solubility of a supercritical carbon dioxide is a property like a non-polar organic solvent, there is selectivity in the dissolution engine performance of a supercritical carbon-dioxide simple substance the 1st. Therefore, although dissolution removal of dissolution removal of the low-molecular organic substance, fats and oils, a wax, etc. is possible, it is the problem that a cleaning effect is low to removal of metal contaminations, such as a metal metallurgy group oxide of ionicity.

In order for lift off to remove a heavy-metal contamination in the 2nd, when the chemical which has the etching force to a supercritical carbon dioxide, and the chemical which has oxidizing power are added, the membrane structure of the porosity low dielectric constant film is the problem that etch thru/or oxidize, change and a dielectric constant becomes high. Moreover, it embeds, wiring is also etched, wiring resistance increases, and there is also a problem formed in the porosity low dielectric constant film of causing wiring delay.

Thus, it was difficult to be able to remove a heavy-metal-contamination object certainly, holding membraneous quality and membrane structure by the washing approach by the conventional supercritical carbon dioxide without changing the membraneous quality of the porosity low dielectric constant film.

[0019]

Then, the purpose of this invention is offering the washing approach which washes and purifies the washed body by which metal contamination was carried out, without doing damage to the washed body. For example, when it is what the washed body embeds in the porosity low dielectric constant film, and has wiring, It is washing and purifying the washed body which was formed in the porosity low dielectric constant film and by which metal contamination was carried out, without having embedded and doing damage to wiring, without changing the membraneous quality of the porosity low dielectric constant film, membrane structure, etc.

[0020]

[Means for Solving the Problem]

In order that this invention person may solve the above-mentioned purpose, in case a supercritical carbon dioxide washes the washed bodies by which metal contamination was carried out, such as porosity low dielectric constant film after CMP, in the process which continued research It found out that a heavy-metal-contamination object could be washed and removed certainly, and the washed body could be dried by carrying out minute amount addition of an organic acid or the chelating agent as a washing assistant beforehand at supercritical fluid, for example, a supercritical carbon dioxide, and carrying out washing processing of the washed body using it as a penetrant remover.

[0021]

Since the permeability to the detailed section is higher than a liquid, supercritical fluid can be easy to accompany an organic acid or a chelating agent to between fine structure objects, such as a hole of the porosity low dielectric constant film, and a heavy-metal-contamination object, thereby, can catch a heavy-metal-contamination object, and can make it remove. Moreover, since the consistency is higher than a gas, supercritical fluid can remove the removed heavy-metal-contamination object easily, and can flush it.

Since the washing assistant is used, it does not arise that it is not necessary to add the chemical which has an etching operation, a wiring metallic material is eaten away like before, and wiring resistance increases.

[0022]

In the approach of washing the washed body with which metal contamination of the washing approach (henceforth the 1st invention approach) concerning this invention is carried out based on above-mentioned knowledge in order to attain the above-mentioned purpose by supercritical fluid,

It is characterized by having the washing process which the supercritical fluid which added the organic acid or the chelating agent with the predetermined appending rate as a washing assistant is used as a penetrant remover, and the washed body is contacted to the supercritical fluid which added the washing assistant, and is washed.

[0023]

In the suitable embodiment of this invention approach, it has the process which gasifies supercritical fluid and dries the washed body following a washing process.

Moreover, in the another suitable embodiment of this invention approach, it has the rinse process which supplies only supercritical fluid and performs rinse washing to the washed body, and the process which subsequently gasifies supercritical fluid and dries the washed body following a washing process.

[0024]

In the approach of washing the washed body with which metal contamination of the washing approach (henceforth the 2nd invention approach) concerning this invention which uses 1 tub type washing / dryer which has washing/desiccation chamber of one tub is carried out by supercritical fluid,

The process which uses 1 tub type washing / dryer which has washing/desiccation chamber of one tub, adds and supplies an organic acid or a chelating agent to supercritical fluid with a predetermined appending rate as a washing assistant at washing/desiccation chamber which holds the washed body, and washes the washed body,

Subsequently, the process which carries out rinse washing of the washed body, permuting the supercritical fluid which supplied only supercritical fluid to washing/desiccation chamber, and added the washing assistant by supercritical fluid,

Subsequently, the process which supercritical fluid is gasified and removed [process] and dries the washed body

It **** and is characterized by performing washing processing and desiccation processing one by one within washing/desiccation chamber of one tub.

[0025]

It dissolves in supercritical fluid, such as a supercritical carbon dioxide, good, and the conditions of the organic acid which can be used as a washing assistant, or a chelating agent are stable under the pressure beyond the critical condition of supercritical fluid, and temperature.

As an organic acid which can be used as a washing assistant by the 1st and 2nd invention approaches, although there are oxalic acid, a malonic acid, a citric acid, a succinic acid, a malic acid, etc., a citric acid and a malic acid are desirable as an organic acid which is stabilized and catches especially a heavy-metal-contamination object certainly.

[0026]

moreover, as a chelating agent which can be used by the 1st and 2nd invention approaches Ethylenediaminetetraacetic acid (EDTA), a diethylenetriamine pentaacetic acid (DTPA), The transformer-cyclohexane -1, 2-diamine tetraacetic acid (CyDTA), Nitrilotriacetic acid (NTA), an IMINONI acetic acid (IDA), TORIETANO, RUAMIN (TEA), 1, 2-cyclohexane diamino tetraacetic acid (CDTA), They are a diethylene triamino 5 methylene phosphoric acid (DTPMP), a hydroxyethyl NIRIN acid (HEDP), an acetylacetone derivative, 1, 1, 1, 5 and 5, the 5-6 fluoride -2, 4-2,4-pentanedione, etc. Especially the chelating agent that is stabilized and catches a heavy-metal contamination certainly is a diethylenetriamine pentaacetic acid (DTPA),

triethanolamine (TEA), 1, 2-cyclohexane diamino tetraacetic acid (CDTA), a diethylene triamino 5 methylene phosphoric acid (DTPMP) and 1, 1, 1, 5 and 5, the 5-6 fluoride -2, or 4-2,4-pentanedione.

[0027]

It may be hard to dissolve an above-mentioned organic acid or an above-mentioned chelating agent in a non-polar solvent like a supercritical carbon dioxide. When it is hard to dissolve, even if it mixes an above-mentioned organic acid or an above-mentioned chelating agent directly to a supercritical carbon dioxide, it is difficult to demonstrate the washing engine performance to the heavy-metal-contamination object of an organic acid or a chelating agent.

Then, by adding to supercritical fluid by making a polar organic solvent into a compatible agent, an organic acid or a chelating agent can be stabilized and dissolved in a supercritical carbon dioxide at the pressure and temperature beyond a critical condition, a complexing operation or a chelate effect can be demonstrated, and the washing engine performance of a supercritical carbon dioxide can be raised.

The addition to the supercritical fluid of a polar organic solvent is 30% or less 10% or more.

[0028]

As such a polar organic solvent, a methanol, ethanol, isopropanol, Alcohols, such as ethylene glycol and a glycerol, an acetone, a methyl ethyl ketone, Lactone, such as ketones, such as methyl isopropyl ketone, and gamma-butyrolactone Nitril, such as ester, such as methyl lactate and ethyl lactate, an acetonitrile, and N-methyl pyrrolidine Ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, A diethylene glycol, the diethylene-glycol monomethyl ether, Diethylene glycol monoethyl ether, the triethylene glycol monomethyl ether, Sulfoxides, such as sulfones, such as ether, such as diethylene-glycol wood ether and dipropylene glycol wood ether, and a sulfolane, and dimethyl sulfoxide, are mentioned. In these, ether, such as the diethylene-glycol monomethyl ether, diethylene glycol monoethyl ether, and dipropylene glycol monomethyl ether, is used especially suitably.

[0029]

Since a washing assistant has critical temperature and the critical pressure higher than a carbon dioxide when using a carbon dioxide as supercritical fluid, in the critical temperature and the critical pressure of an interflow object with a supercritical carbon dioxide, the critical temperature and the critical pressure of a carbon dioxide become high.

Then, it is desirable to hold the temperature and the pressure of a supercritical carbon

dioxide highly to 40 degrees C and 10MPa(s), respectively so that a washing assistant may dissolve to a supercritical carbon dioxide well.

the concentration of an organic acid or a chelating agent — 40 degrees C and the supercritical carbon dioxide of 8MPa — less than [more than 0.01mol%2mol%] — it is a density range not more than more than 0.05mol%1mol% preferably. When an organic acid or chelating agent concentration is lower than 0.01-mol%, it is difficult to remove a heavy-metal-contamination object completely, and when higher than two-mol%, an organic acid or a chelating agent does not dissolve into a supercritical carbon dioxide, but there is a possibility of depositing on the washed body.

[0030]

[Embodiment of the Invention]

With reference to an accompanying drawing, the example of an operation gestalt is given to below, and the gestalt of operation of this invention is explained to it at concrete and a detail.

The example 1 of an operation gestalt

This example of an operation gestalt is an example of the operation gestalt of the washing approach concerning the 1st and 2nd invention approaches, and drawing 1 R> 1 is a flow sheet which shows the configuration of washing/dryer used in case the approach of this example of an operation gestalt is enforced.

First, with reference to drawing 1 , the configuration of washing/dryer used in case the approach of this example of an operation gestalt is enforced is explained. Washing / dryer 10 is washing/dryer of the batch type which carries out washing/desiccation processing of the washed body like the wafer which has the low dielectric constant film by which heavy metal pollution was carried out as shown in drawing 5 (c) and drawing 6 (c).

The chamber 16 which washing / dryer 10 has opening 12 in the upper part as shown in drawing 1 , and has the processing room 14 which contains the washed body W by which carrying-in appearance is carried out through opening 12 inside, The lid 18 which seals opening 12, and the fluid source of supply 20 which supplies a processing fluid to the processing room 14, A fluid supply means to introduce a processing fluid in the processing room 14 from the fluid source of supply 20, It has a washing assistant supply means to add a washing assistant in a processing fluid from the washing assistant source of supply 22, a polar organic solvent supply means to add a polar organic solvent in a processing fluid from the polar organic solvent source of supply 24, and a fluid discharge means to discharge the processing fluid with which processing of the washed body was presented from the processing room 14.

[0031]

A processing fluid means the supercritical fluid used as a penetrant remover which removes the heavy-metal-contamination object of the washed body W. Moreover, a washing assistant means an organic acid or a chelating agent. In addition, the supercritical fluid which added the washing assistant may be called processing fluid.

In this example of an operation gestalt, a supercritical carbon dioxide is used as supercritical fluid.

[0032]

Carrying-in appearance of the washed body W is carried out to the processing room 14 through opening 12. Between the opening edge of the opening 12 of the processing room 14, and the lid 18, O ring 26 is arranged as a seal member so that opening 12 can be sealed with a lid 18. With the bolting implements 28, such as ****, a lid 18 is connected with the processing room 14, and seals the processing room 14. That is, the interior of the processing room 14 can be changed into the condition of having been sealed completely, by binding the lid 18 through O ring 26 tight, and binding tight with an ingredient 28.

Moreover, inside the processing room 14, the washed body maintenance cassette 30 for laying and holding two or more washed bodies W can be arranged.

[0033]

A fluid supply means consists of the pressure and a temperature control means 32 to control a processing fluid to a predetermined pressure and predetermined temperature, a cross valve 34, and a fluid supply port 36 arranged in the processing room 14, and introduces the processing fluid controlled by the pressure and the temperature control means 32 by a predetermined pressure and temperature through the cross valve 34 and the fluid supply port 36 from the fluid source of supply 20 in the processing room 14.

The pressure and the temperature control means 32 consist of [temperature] in-line heaters which carry out a temperature up in the booster pump and processing fluid which carry out the pressure up of the processing fluid.

[0034]

The washing assistant supply means 38 is equipped with a pump etc., and supplies a washing assistant to a processing fluid by the supply line 42 through the closing motion valve 40 from the washing assistant source of supply 22.

The polar organic solvent supply means 44 is equipped with a pump etc., and supplies a polar organic solvent to a processing fluid by the supply line 40 through the closing motion valve 46 from the polar-solvents source of supply 24.

It connects with the cross valve 34 equipped with the feed hopper 48, and a supply line

42 adds the polar organic solvent or washing assistant of the specified quantity in a processing fluid through the fluid supply port 36 by opening adjustment of a cross valve 34.

[0035]

The fluid discharge means consists of a fluid discharge port 50 established in the processing room 14, an exhaust-gas-pressure valve 52, and an effluent liquor decollator 54 connected to the fluid discharge port 50 through the exhaust-gas-pressure valve 52.

[0036]

The exhaust-gas-pressure valve 52 will be opened if the internal pressure of the processing room 14 becomes more than a setting pressure, and it has the function which discharges the processing fluid introduced in the processing room 14. That is, the exhaust-gas-pressure valve 52 can maintain the pressure in the processing room 14 at a predetermined pressure.

The effluent liquor decollator 54 is vapor-liquid-separation equipment, and the discharged supercritical carbon dioxide (a washing assistant is included) is divided into a gas component and a liquid component by reducing a pressure to atmospheric pressure. A supercritical carbon dioxide evaporates a gas component and it is recovered by the gas recovery system (not shown) as exhaust gas. A washing assistant etc. is separated as a liquid and liquid components are collected as effluent liquor.

The collected exhaust gas is a carbon dioxide etc. and can also be reused. Moreover, the collected effluent liquor is reusable similarly.

[0037]

Furthermore, the side attachment wall of a chamber 16 is equipped with a heating means 56 to heat the processing fluid introduced in the processing room 14, and to hold to predetermined temperature.

The heating means 56 is equipped with the temperature controller 58 which consists of heating media like heating wire, controls the power supplied to heating wire from the power source (not shown) prepared in the exterior of the processing room 14, and controls the temperature of the heating means 56 to predetermined temperature.

[0038]

Although this washing / dryer 10 is equipment which washes two or more washed bodies W by the batch type, washing/dryer of single-wafer-processing processing are also the same configuration as this washing / dryer 10, and a process flow fundamentally, and although it ends with a small processing room, a throughput falls.

[0039]

Next, how to follow the approach of this example of an operation gestalt using

above-mentioned washing / dryer 10, and wash / dry the washed body W is explained. In this example of an operation gestalt, as the washed body W shows drawing 5 (c) or drawing 6 (c), it is the wafer which has the laminated structure by which heavy metal contamination was carried out, and a methanol is used as an organic acid, for example, a citric acid, and a polar organic solvent as a washing assistant.

[0040]

First, the washed body maintenance cassette 30 which held two or more washed bodies W from the opening 12 of the processing room 14 is contained in the processing room 14. Then, a lid 18 is shut, the processing room 14 is changed into a sealing condition, and a supercritical carbon dioxide is introduced in the processing room 14 from the processing fluid source of supply 20.

[0041]

If 7.38 or more MPas are pressurized and a carbon dioxide is heated at 31.1 degrees C or more on the occasion of installation, since it will be in a supercritical condition, the pressure up of the pressure is preferably carried out for a carbon dioxide to 10MPa(s) with a pressure and the temperature control means 32 from the processing fluid source of supply 20 at 7.38 or more MPas, the temperature up of the temperature is preferably carried out to 40 degrees C, and it is introduced into 31.1 degrees C or more in the processing room 14 through a supply port 36.

To coincidence, the supercritical carbon dioxide introduced in the processing room 14 by the heating means 56 is heated, and the temperature of the supercritical carbon dioxide in the processing room 14 is maintained at 40 degrees C with a temperature controller 58 at it.

A supercritical carbon dioxide is maintained to the temperature of 40 degrees C, and the pressure of 10MPa for raising the solubility of a washing assistant and raising the washing engine performance of a supercritical carbon dioxide.

[0042]

With installation of a supercritical carbon dioxide, opening of the opening of a cross valve 34 is adjusted and carried out, and a washing assistant is added from the washing assistant source of supply 22 with a predetermined appending rate to a supercritical carbon dioxide through a feed hopper 48. In this example of an operation gestalt, an appending rate is 1 % of the weight.

[0043]

A temperature controller 58 performs temperature control of a supercritical carbon dioxide. If the internal pressure of the processing room 14 becomes more than a constant pressure, the exhaust-gas-pressure valve 52 will open and a supercritical

carbon dioxide and a washing assistant will be discharged out of a system via the effluent liquor decollator 54.

Thus, it is possible to keep constant the pressure in the processing room 14 and temperature by discharging suitably the supercritical carbon dioxide with which it filled up in the processing room 14.

the supercritical carbon dioxide which added the washing assistant — the washed body W — predetermined time — for example, it is immersed for 10 minutes and a heavy-metal-contamination object is removed. Subsequently, while the washed body W had been made immersed in the supercritical carbon dioxide which added the washing assistant, the closing motion valve 40 is stopped, supply of a washing assistant is suspended, only a supercritical carbon dioxide is supplied to the processing room 14 as a rinse, and a washing assistant is discharged, thinning washing assistant concentration gradually. It is separated by the effluent liquor decollator 54 and recovery playback of the mixed waste fluid of a carbon dioxide and a washing assistant is carried out if needed.

[0044]

Then, the pressure of the processing room 14 is lowered, and if a carbon dioxide is discharged and it cools, the washed body W will be fulfilled by the gaseous carbon dioxide, and will be dried. In supercritical drying, a pressure is decompressed to atmospheric pressure, holding temperature at 31.1 degrees C or more, after holding temperature at 40 degrees C, holding a pressure to 10MPa(s) and washing, when a carbon dioxide is used, for example as supercritical fluid. Then, temperature is lowered from 31.1 degrees C or more to a room temperature, for example, 20 degrees C.

By this, the washed body W in the processing room 14 will be in dryness. Thus, it becomes possible to make it dry, without destroying the fine structure of the washed body W which has the fine structure like the hole of the porosity low dielectric constant film by passing through supercritical drying.

By passing through the above process, the heavy-metal-contamination object adhering to the washed body W can be removed, and the pure washed body W can be acquired.

[0045]

The example 1 of an experiment

Cu atoms are 1013 atom/cm² before washing as an example 1 of an experiment. When washing/desiccation processing of the wafer which has the laminated structure shown in drawing 6 (c) which was carrying out extent adhesion is carried out by the approach of this example of an operation gestalt, as it is shown in drawing 2, it is the coating weight of Cu atom of a wafer 1010 atom/cm² It could decrease to extent and sufficient

heavy-metal-contamination removal was able to be attained.

When a washing assistant was not added but washing/desiccation processing of the same wafer as the example 1 of an experiment was carried out by using only a supercritical carbon dioxide as a processing fluid as an example of a comparison, the coating weight of Cu atom of a wafer is 1012 atom/cm². It is extent and the coating weight of Cu atom was almost changeless washing before.

[0046]

The example 2 of an experiment

Moreover, it is after washing, the structure before wiring layer membrane formation (presentation) was investigated using infrared absorption spectrometry, and the presentation change before and behind washing was indicated to be the structure before washing of the porosity low dielectric constant film when washing the porosity low dielectric constant film before wiring layer membrane formation by the washing approach of the example 1 of an operation gestalt (presentation) shown in drawing 6 (a) to drawing 3.

The wave number (cm⁻¹) of an infrared absorption spectrum is taken along a horizontal axis, it takes an absorbance (arbitration graduation) along an axis of ordinate, and drawing 3 shows the graph which shows the relation between the wave number (cm⁻¹) of the infrared absorption spectrum before washing on the upper case, and an absorbance, and the graph which shows the relation between the wave number (cm⁻¹) of the infrared absorption spectrum after washing in the lower berth, and an absorbance. In addition, although the absorbance before and behind washing is the same, in order to show the location of the peak wave number clearly, it dissociates up and down and it is displayed.

[0047]

Si-O, Si-H, Si-OH, Si-CH₃ which are before and after washing and constitute the porosity low dielectric constant film so that drawing 3 may show Change was not looked at by association of C-H etc. Therefore, since are before and after washing and presentation change has not arisen, i.e., it is before and after washing and is changeless in the structure of the low dielectric constant film, it can be judged that that a hole is crushed and a dielectric constant changes has not arisen.

Without it seeming that the porosity low dielectric constant film passes a gas-liquid interface, and the porous hole was crushed on the occasion of washing and desiccation like before since the gas-liquid interface was not generating to a supercritical carbon dioxide so that the examples 1 and 2 of an experiment might show, the heavy-metal-contamination object was removed and it has checked that it could be

made to dry.

[0048]

In addition, if the closing motion valve 46 is opened wide and it pours into supercritical fluid via the supply line 42 and the cross valve 34 from the polar organic solvent source of supply 24 with the polar-solvents supply means 44 before pouring a washing assistant into a supercritical carbon dioxide, the solubility of a washing assistant can be raised further. The addition ratio of a polar organic solvent is 20% or less more than per %.

[0049]

Although chemical mechanical polishing (Chemical Mechanical Polishing: CMP) was made into the example and explained as the polish approach of a metal membrane, as the polish approach, it is not restricted only to CMP. For example, the heavy metal contamination generated in electrolytic polishing (Electro Chemical Polishing : ECP) etc. can be similarly removed by the washing approach of this invention, without changing the structure of the porosity low dielectric constant film.

[0050]

Although the wafer equipped with the wiring structure using the porosity low dielectric constant film formed by the production process of LSI as the washed body is made into the example by the approach of this example of an operation gestalt, it is applicable also like many of microstructures of others which are formed by the production process of LSI.

moreover — when it is the micro machine which has the moving part which consists of Ayr bridge structure and the approach of this example of an operation gestalt was applied by use as the wash body that by which heavy metal contamination was carried out , without the Ayr bridge front face is eat away like before after washing — moreover , the substrate of the Ayr bridge — also stick — it checked that there was nothing and a heavy metal contamination object could be removed .

[0051]

The example 2 of an operation gestalt

Although washing/desiccation processing of the washed body by which is the wafer which embedded on the porosity low dielectric constant film, and prepared wiring, and heavy metal contamination was carried out is carried out in the example 1 of an operation gestalt, this invention approach is applicable also to the washed bodies other than these.

This example of an operation gestalt is an example of an operation gestalt which applied the washing approach concerning the 1st and 2nd invention approaches to weak

washing of the electrode structure of structure which has the pattern of a high aspect ratio shown in drawing 4 prepared in the large-scale integrated circuit. It is the sectional view of each process at the time of (c) forming electrode structure from drawing 4 (a), respectively.

In this example of an operation gestalt, as shown in drawing 4 (a), after forming an insulator layer thin as the 1st layer 64 on the Si substrate 62 first, one by one, the 2nd layer (insulator layer) 66, the 3rd layer (metal membrane) 68, and the 4th layer (insulator layer) 70 are formed, and a laminated structure is formed.

The resist film is applied on the 4th layer 70, photolithography processing is performed, and the resist mask 72 is formed.

Then, the 4th layer 70, the 3rd layer 68, and the 2nd layer 64 are etched by the dry etching method from on the resist mask 72, and as shown in drawing 4 (b), the electrode structure 74 of the detailed pattern which consists of the 3rd layer (metal membrane) 68 is formed on the 1st layer 64 of the Si substrate 62.

[0052]

By the way, since the etch residue and the heavy-metal-contamination object have adhered to the side attachment wall of the 2nd layer 64 and the 3rd layer 68 as shown in drawing 4 (b), it is necessary to remove.

Although the residue of an organic component like resist material is removable at a resist removal process, a heavy-metal-contamination object is unremovable. Then, although it is necessary to wash and remove a heavy-metal-contamination object apart from a resist removal process, in washing by the usual penetrant remover, the aspect ratio of a pattern is large and the pattern of the electrode structure 74 collapses.

Then, without collapsing a detailed pattern by using washing / dryer 10, adding an organic acid or a chelating agent as a washing assistant to supercritical fluid, for example, a supercritical carbon dioxide, like the example 1 of an operation gestalt, and carrying out washing processing of the electrode structure 74, as shown in drawing 4 (c), the detailed electrode structure 74 which removed the heavy-metal-contamination object can be formed.

[0053]

[Effect of the Invention]

By having the washing process which the supercritical fluid which added the organic acid or the chelating agent with the predetermined appending rate as a washing assistant is used as a penetrant remover, and the washed body is contacted to the supercritical fluid which added the washing assistant, and is washed according to the 1st invention approach Without damaging the fine structure of the washed bodies, such as a hole of

the porosity low dielectric constant film, according to a metal prehension operation of an organic acid or a chelating agent, a heavy-metal-contamination object can be washed and removed certainly, and the washed body can be dried.

Moreover, a heavy-metal-contamination object can be washed and removed, without doing damage to a microstructure, also when the 1st and 2nd invention approaches are applied to washing of the washed body which consists of a microstructure of a beam configuration like the Ayr bridge of a micro machine, or a cantilever.

According to the 2nd invention approach, batch processing of washing of the washed body polluted with the heavy-metal-contamination object, purification, and the desiccation can be carried out with washing/dryer of 1 tub type.

Moreover, by the 1st and 2nd invention approaches, since it is not necessary to add the chemical which has an etching operation or the oxidation, it embeds [which was formed in the porosity low dielectric constant film, for example], wiring is eaten away, and the problem of wiring resistance going up does not arise.

[Brief Description of the Drawings]

[Drawing 1] It is the flow sheet which shows the configuration of washing/dryer used in case the approach of the example 1 of an operation gestalt is enforced.

[Drawing 2] Drawing 2 is a bar graph which shows the result of having carried out counting of the number of the heavy-metal contaminations before and behind washing of the washed body in the example 1 of an experiment, and the example of a comparison (particle).

[Drawing 3] The wave number (cm⁻¹) of an infrared absorption spectrum is taken along a horizontal axis, an absorbance (arbitration graduation) is taken along an axis of ordinate, and the graph which shows the relation between the wave number (cm⁻¹) of the infrared absorption spectrum before washing and after washing and an absorbance to an upper case and the lower berth, respectively is shown.

[Drawing 4] It is the sectional view of each process at the time of (c) forming electrode structure from drawing 4 (a), respectively.

[Drawing 5] It is a sectional view explaining each process at the time of the porosity low dielectric constant film being used for (c) from drawing 5 (a), respectively, and forming metal wiring and a metal plug according to a single DAMASHIN process.

[Drawing 6] It is a sectional view explaining each process at the time of the porosity low dielectric constant film being used for (c) from drawing 6 (a), respectively, and a dual DAMASHIN process explaining metal wiring and a metal plug.

[Description of Notations]

10 [.. Chamber,] Washing/dryer, 12 .. Opening, 14 .. A processing room, 16 18 [..

Polar-solvents source of supply,] A lid, 20 .. A fluid source of supply, 22 .. A washing assistant source of supply, 24 26 An O ring, 28 .. A bolting implement, 30 .. Washed body maintenance cassette, 32 A pressure and a temperature control means, 34 .. A cross valve, 36 .. Fluid supply port, 38 A washing assistant supply means, 40 .. A closing motion valve, 42 .. Supply line, 44 [.. Fluid discharge port,] A polar-solvents supply means, 46 .. A closing motion valve, 48 .. A feed hopper, 50 52 [.. Temperature controller,] An exhaust-gas-pressure valve, 54 .. An effluent liquor decollator, 56 .. A heating means, 58 62 Si substrate, 64 .. The 1st layer (thin insulator layer), 66 .. The 2nd layer (insulator layer), 68 The 3rd layer (metal membrane), 70 .. The 4th layer (insulator layer), 72 .. Resist mask, 74 Electrode structure, 76 .. The substrate film, 78 .. Etching mask layer, 80 The porosity low dielectric constant film, 82 .. A contact hole, 84 .. Wiring gutter, 86 [.. Embedding wiring,] A reaction prevention layer, 88 .. A metal membrane, 90 .. A metal plug, 92 93 A heavy-metal-contamination object, 94 .. The substrate film, 96 .. The 1st porosity low dielectric constant film, 98 The 1st etching mask layer, 100 .. The 2nd porosity low dielectric constant film, 102 [.. A reaction prevention layer, 112 / .. 114 A metal membrane, 116 / .. A metal plug, 118 / .. Embedding wiring, 120 / .. Heavy-metal-contamination object] 104 The 2nd etching mask layer, 106 .. A contact hole, 108 .. A wiring gutter, 110

TECHNICAL FIELD

[Field of the Invention]

This invention relates to the optimal washing approach for washing of the wafer which was formed with the application of the washed body polluted with metals, such as a tungsten, aluminum, and copper, especially CMP, or ECP and which embeds and has wiring in more detail about the washing approach.

[0002]

PRIOR ART

[Description of the Prior Art]

At the process which forms metal wiring of semiconductor devices, such as a transistor, after forming the metal membrane for metal wiring formation conventionally, on a metal membrane, the resist film is formed, patterning of the resist film is carried out, and an etching mask is formed. Then, a metal membrane is etched by the dry etching method from on an etching mask, and metal wiring is formed.

Moreover, at the process which forms the metal plug which connects vertical wiring

with the wiring structure of a semiconductor device, after forming the metal membrane for metal plug formation and embedding a contact hole on the insulator layer in which the contact hole was formed, etchback of the whole metal membrane surface is carried out, and the metal plug is formed.

[0003]

By the way, in case the metal membrane on an insulator layer is ground and removed henceforth [a 0.18 micron device generation] on the occasion of formation of embedding metal wiring and a metal plug as high integration of a device, high aspect-ization, etc. progress in recent years, they are chemical mechanical polishing (ChemicalMechanical Polishing : CMP) and electrolytic polishing (Electro Chemical Polishing).

: It is coming to apply ECP.

[0004]

For example, in wiring formation of a semiconductor device, the so-called DAMASHIN process which grinds the metal layer on an insulator layer, removes by CMP or ECP, embeds, and forms metal wiring is used.

a DAMASHIN process — first — reactive ion etching (RIE) — law etc. — SiO₂ on a wafer etc. — a layer insulation layer is etched and a wiring gutter is formed. Subsequently, metal membranes, such as aluminum film and a copper film, are formed by the CVD method, or a spatter or the galvanizing method all over a wafer, for example, a wiring gutter is embedded, CMP and ECP grind and remove the metal membrane on a layer insulation layer continuously, it embeds at wiring Mizouchi, and metal wiring is formed.

[0005]

Moreover, similarly formation of a metal plug has applied CMP. first, SiO₂ etc. — a layer insulation layer — reactive ion etching (RIE) — a connection hole is formed by law etc. Subsequently, for example, the titanium film, the titanium nitride film, the tantalum nitride film, etc. are formed all over a wafer including the porous wall of a connection hole as an adhesion layer with a spatter or a CVD method, for example, the tungsten film is continuously formed on an adhesion layer with a CVD method, and a connection hole is embedded. Subsequently, by CMP, the tungsten film and adhesion layer on a layer insulation layer are ground, and a metal plug is formed in a connection hole.

[0006]

By the way, by the CMP method of the conventional metal membrane, since the polished surface of a metal membrane was washed after laying the wafer on the rotating polish plate (it is also called a platen) and grinding the metal membrane on a wafer

using a slurry-like abrasive material, there were the following problems.

I hear that it is easy to generate a blemish (scratch) on that a lot of particle set to the 1st from the metallic oxide originating in an abrasive material slurry, a ceramic, etc. remains on a wafer front face, and a wafer front face, and it is shown in them.

It is concern that metal contamination of the wafer front face is carried out with the metallic oxide contained in an abrasive material slurry the 2nd. If heavy metal contamination occurs on an interlayer insulation film or in an interlayer insulation film especially, since leak between wiring will be caused, it becomes a very serious problem. Also when the metal membrane on an interlayer insulation film is ground by ECP, the same heavy metal contamination poses a problem.

[0007]

On the other hand, for improvement in the speed of LSI, it is indispensable to reduce the capacity between wiring. Then, in order to reduce the capacity between wiring, the low dielectric constant film is used as an interlayer insulation film during wiring.

Furthermore, in order to form the interlayer insulation film of much more a low dielectric constant, the attempt which makes porosity membraneous quality of not only selection of a film ingredient but an interlayer insulation film has accomplished.

[0008]

Here, how to use the porosity low dielectric constant film as an interlayer insulation film, embed according to a single DAMASHIN process with reference to drawing 5 , and form metal wiring and a metal plug is explained. It is a sectional view explaining each process at the time of the porosity low dielectric constant film being used for (c) from drawing 5 (a), and forming metal wiring and a metal plug according to a single DAMASHIN process.

First, as shown in drawing 5 (a), through the etching mask layer 78, the porosity low dielectric constant film 80 is formed on the substrate film 76, and the contact hole 82 and wiring gutter 84 which are arrived at subsequently to the substrate film 76 at the low dielectric constant film 80 are formed.

Subsequently, as shown in drawing 5 (b), the metal membrane 88 for metal plug formation is continuously formed the reaction prevention layer 86 and formed in the wall of a contact hole 82 and a wiring gutter 84 on the low dielectric constant film 80, and a contact hole 82 and a wiring gutter 84 are embedded.

Subsequently, as shown in drawing 5 (c), while giving CMP, grinding a metal membrane 88 and exposing the low dielectric constant film 80, the metal plug 90 and the embedding wiring 92 are formed.

[0009]

By the way, as shown after CMP at drawing 5 (c), the heavy-metal-contamination object 93 produced from the abrasive material slurry of metal membrane residue or CMP is generated on the low dielectric constant film 80 or in the low dielectric constant film 80. If it produces commercially while metal contamination of the low dielectric constant film 80 had been carried out with these heavy-metal-contamination objects 93, since leak between wiring etc. will occur, it is required to remove the heavy-metal-contamination object 93 and to defecate the low dielectric constant film 80.

[0010]

Moreover, in case it embeds according to a dual DAMASHIN process and wiring is formed, as shown in drawing 6 (a), the 1st porosity low dielectric constant film 96, the 1st etching mask layer 98, the 2nd porosity low dielectric constant film 100, and the 2nd etching mask layer 102 are formed one by one on the substrate film 94. Then, the contact hole 104 which reaches the substrate film 94, a contact hole 106, and a wiring gutter 108 are formed using the etching mask formed from the 1st etching mask layer 98 and the 2nd etching mask layer 102. Subsequently, the reaction prevention layer 110 is formed in the wall of contact holes 104 and 106 and a wiring gutter 108.

As shown in drawing 6 (b), the metal membrane 112 for wiring and metal plug formation is formed on the 2nd etching mask layer 102, and contact holes 104 and 106 and a wiring gutter 108 are embedded.

Subsequently, as shown in drawing 6 (c), while giving and grinding CMP in a metal membrane 112 and the 2nd etching mask layer 102 and exposing the 2nd porosity low dielectric constant film 100, the metal plugs 114 and 116 and the embedding wiring 118 are formed.

[0011]

By the way, as shown after CMP at drawing 6 (c), the heavy-metal-contamination object 120 produced from metal membrane residue or an abrasive material slurry is generated on the 2nd porosity low dielectric constant film 100 or in the film.

If it produces commercially while metal contamination had been carried out with these heavy-metal-contamination objects, since leak between wiring etc. will occur, it is required to remove a heavy-metal-contamination object and to defecate the 2nd porosity low dielectric constant film 100.

In addition, it is a sectional view explaining each process at the time of the porosity low dielectric constant film being used for (c) from drawing 6 (a), respectively, and forming metal wiring and a metal plug according to a dual DAMASHIN process.

[0012]

Although these heavy-metal-contamination object had to be removed in order to

manufacture LSI devices which are not produced, such as leak between wiring, as stated above, there were the following problems which should be solved on that occasion.

Usually, in removing heavy metal, wet washing using water is performed as wash water, and, subsequently it is dry. However, since the differential pressure of the pressure of a penetrant remover and atmospheric pressure occurs in a gas-liquid interface when penetrant removers, such as water with large surface tension, frequent the hole of the porosity low dielectric constant film on the occasion of washing, the hole of the porosity low dielectric constant film is crushed, membraneous quality changes, and the dielectric constant of the low dielectric constant film becomes high in many cases. Now, the effectiveness which uses the porosity low dielectric constant film declines.

[0013]

What is necessary is to use a fluid with small surface tension and just to do washing/desiccation of, in order to make it a hole not crushed. For example, although the surface tension of water is about 72 dyn/cm, since the surface tension of a methanol is about 23 dyn/cm, after carrying out backwashing by water rather than it makes it dry immediately after carrying out backwashing by water, a methanol permutes water and the direction subsequently dried tends to suppress change of the membraneous quality of the low dielectric constant film.

However, since it is not so small as the surface tension of a methanol can also be disregarded, a hole is crushed to some extent. Therefore, change of membraneous quality cannot be prevented completely and it does not become a perfect problem solving.

[0014]

It is drying after it makes it dry after washing using the fluid whose surface tension is zero as a rinse or carrying out a rinse with such a liquid, in order to make it the hole of the porosity low dielectric constant film not crushed, or surface tension permutes a rinse by the fluid of zero.

Surface tension can mention supercritical fluid as a fluid of zero. A supercritical condition is one of the condition phases which the matter takes under the critical temperature of a proper, and the critical pressure to the matter, and supercritical fluid means the fluid in a supercritical condition.

While the solvent power of supercritical fluid over other liquids and solid-states is almost equivalent to the fluid of a liquid condition, the viscosity is remarkably small and it has the unique property in which a diffusion coefficient is very large. If it puts in another way, it can be said to be a liquid with a gaseous property.

Therefore, since supercritical fluid does not form a gas-liquid interface, surface tension

becomes zero. Then, if the washed body is dried in the state of supercritical, since surface tension does not exist, the differential pressure by generating of a gas-liquid interface will be produced at all.

[0015]

Since supercritical fluid will be promptly gasified if a pressure turns into below the critical pressure, after washing using supercritical fluid, supercritical fluid can be easily emitted by decompressing.

Therefore, after the porosity low dielectric constant film washes the substrate exposed to a front face, After washing by the penetrant remover directly from a penetrant remover and carrying out a rinse by the rinse subsequently Or after carrying out a rinse and another liquid permutes a rinse, the liquid adhering to a substrate is easily removable by contacting the substrate to which the penetrant remover, the rinse, or another liquid has adhered to the supercritical fluid in a proof-pressure container, and dissolving these liquids in supercritical fluid.

Subsequently, a substrate can be picked out from a proof-pressure container in atmospheric air by reducing the pressure in a proof-pressure container below to the critical pressure, maintaining the temperature in a proof-pressure container more than critical temperature, and gasifying supercritical fluid.

Since the surface tension of supercritical fluid is very small, in case supercritical fluid is removed from a substrate front face, the stress given to the microstructure of a wafer, for example, the hole of a pattern or the porosity low dielectric constant film, with the surface tension is extent which can be disregarded. As [arise / therefore, / on the porosity low dielectric constant film / deterioration] (JP,2000-154273,A)

[0016]

Many matter with which it is checked as supercritical fluid that it will be in supercritical conditions, such as a carbon dioxide, ammonia, water, alcohols, aliphatic saturated hydrocarbon of low molecular weight, benzene, and diethylether, can be used.

In these matter, without putting that handling is easy and the washed body to an elevated temperature, washing / since it says that it can dry, the carbon dioxide with the supercritical temperature near 31.3 degrees C and a room temperature is one of the matter desirable as a penetrant remover.

[0017]

[Patent reference 1]

JP,10-135170,A (drawing 1)

[Patent reference 2]

The patent No. 2574781 official report (drawing 1)

[0018]

EFFECT OF THE INVENTION

[Effect of the Invention]

By having the washing process which the supercritical fluid which added the organic acid or the chelating agent with the predetermined appending rate as a washing assistant is used as a penetrant remover, and the washed body is contacted to the supercritical fluid which added the washing assistant, and is washed according to the 1st invention approach Without damaging the fine structure of the washed bodies, such as a hole of the porosity low dielectric constant film, according to a metal prehension operation of an organic acid or a chelating agent, a heavy-metal-contamination object can be washed and removed certainly, and the washed body can be dried.

Moreover, a heavy-metal-contamination object can be washed and removed, without doing damage to a microstructure, also when the 1st and 2nd invention approaches are applied to washing of the washed body which consists of a microstructure of a beam configuration like the Ayr bridge of a micro machine, or a cantilever.

According to the 2nd invention approach, batch processing of washing of the washed body polluted with the heavy-metal-contamination object, purification, and the desiccation can be carried out with washing/dryer of 1 tub type.

Moreover, by the 1st and 2nd invention approaches, since it is not necessary to add the chemical which has an etching operation or the oxidation, it embeds [which was formed in the porosity low dielectric constant film, for example], wiring is eaten away, and the problem of wiring resistance going up does not arise.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]

However, there were the following problems in the conventional washing approach by the supercritical carbon dioxide.

Since the solubility of a supercritical carbon dioxide is a property like a non-polar organic solvent, there is selectivity in the dissolution engine performance of a supercritical carbon-dioxide simple substance the 1st. Therefore, although dissolution removal of dissolution removal of the low-molecular organic substance, fats and oils, a wax, etc. is possible, it is the problem that a cleaning effect is low to removal of metal contaminations, such as a metal metallurgy group oxide of ionicity.

In order for lift off to remove a heavy-metal contamination in the 2nd, when the chemical which has the etching force to a supercritical carbon dioxide, and the chemical

which has oxidizing power are added, the membrane structure of the porosity low dielectric constant film is the problem that etch thru/or oxidize, change and a dielectric constant becomes high. Moreover, it embeds, wiring is also etched, wiring resistance increases, and there is also a problem formed in the porosity low dielectric constant film of causing wiring delay.

Thus, it was difficult to be able to remove a heavy-metal-contamination object certainly, holding membraneous quality and membrane structure by the washing approach by the conventional supercritical carbon dioxide without changing the membraneous quality of the porosity low dielectric constant film.

[0019]

Then, the purpose of this invention is offering the washing approach which washes and purifies the washed body by which metal contamination was carried out, without doing damage to the washed body. For example, when it is what the washed body embeds in the porosity low dielectric constant film, and has wiring, It is washing and purifying the washed body which was formed in the porosity low dielectric constant film and by which metal contamination was carried out, without having embedded and doing damage to wiring, without changing the membraneous quality of the porosity low dielectric constant film, membrane structure, etc.

[0020]

MEANS

[Means for Solving the Problem]

In order that this invention person may solve the above-mentioned purpose, in case a supercritical carbon dioxide washes the washed bodies by which metal contamination was carried out, such as porosity low dielectric constant film after CMP, in the process which continued research It found out that a heavy-metal-contamination object could be washed and removed certainly, and the washed body could be dried by carrying out minute amount addition of an organic acid or the chelating agent as a washing assistant beforehand at supercritical fluid, for example, a supercritical carbon dioxide, and carrying out washing processing of the washed body using it as a penetrant remover.

[0021]

Since the permeability to the detailed section is higher than a liquid, supercritical fluid can be easy to accompany an organic acid or a chelating agent to between fine structure objects, such as a hole of the porosity low dielectric constant film, and a heavy-metal-contamination object, thereby, can catch a heavy-metal-contamination object, and can make it remove. Moreover, since the consistency is higher than a gas,

supercritical fluid can remove the removed heavy-metal-contamination object easily, and can flush it.

Since the washing assistant is used, it does not arise that it is not necessary to add the chemical which has an etching operation, a wiring metallic material is eaten away like before, and wiring resistance increases.

[0022]

In the approach of washing the washed body with which metal contamination of the washing approach (henceforth the 1st invention approach) concerning this invention is carried out based on above-mentioned knowledge in order to attain the above-mentioned purpose by supercritical fluid,

It is characterized by having the washing process which the supercritical fluid which added the organic acid or the chelating agent with the predetermined appending rate as a washing assistant is used as a penetrant remover, and the washed body is contacted to the supercritical fluid which added the washing assistant, and is washed.

[0023]

In the suitable embodiment of this invention approach, it has the process which gasifies supercritical fluid and dries the washed body following a washing process.

Moreover, in the another suitable embodiment of this invention approach, it has the rinse process which supplies only supercritical fluid and performs rinse washing to the washed body, and the process which subsequently gasifies supercritical fluid and dries the washed body following a washing process.

[0024]

In the approach of washing the washed body with which metal contamination of the washing approach (henceforth the 2nd invention approach) concerning this invention which uses 1 tub type washing / dryer which has washing/desiccation chamber of one tub is carried out by supercritical fluid,

The process which uses 1 tub type washing / dryer which has washing/desiccation chamber of one tub, adds and supplies an organic acid or a chelating agent to supercritical fluid with a predetermined appending rate as a washing assistant at washing/desiccation chamber which holds the washed body, and washes the washed body,

Subsequently, the process which carries out rinse washing of the washed body, permuting the supercritical fluid which supplied only supercritical fluid to washing/desiccation chamber, and added the washing assistant by supercritical fluid,

Subsequently, the process which supercritical fluid is gasified and removed [process] and dries the washed body

It **** and is characterized by performing washing processing and desiccation processing one by one within washing/desiccation chamber of one tub.

[0025]

It dissolves in supercritical fluid, such as a supercritical carbon dioxide, good, and the conditions of the organic acid which can be used as a washing assistant, or a chelating agent are stable under the pressure beyond the critical condition of supercritical fluid, and temperature.

As an organic acid which can be used as a washing assistant by the 1st and 2nd invention approaches, although there are oxalic acid, a malonic acid, a citric acid, a succinic acid, a malic acid, etc., a citric acid and a malic acid are desirable as an organic acid which is stabilized and catches especially a heavy-metal-contamination object certainly.

[0026]

moreover, as a chelating agent which can be used by the 1st and 2nd invention approaches Ethylenediaminetetraacetic acid (EDTA), a diethylenetriamine pentaacetic acid (DTPA), The transformer-cyclohexane -1, 2-diamine tetraacetic acid (CyDTA), Nitrilotriacetic acid (NTA), an IMINONI acetic acid (IDA), TORIETANO, RUAMIN (TEA), 1, 2-cyclohexane diamino tetraacetic acid (CDTA), They are a diethylene triamino 5 methylene phosphoric acid (DTPMP), a hydroxyethyl NIRIN acid (HEDP), an acetylacetone derivative, 1, 1, 1, 5 and 5, the 5-6 fluoride -2, 4-2,4-pentanedione, etc. Especially the chelating agent that is stabilized and catches a heavy-metal contamination certainly is a diethylenetriamine pentaacetic acid (DTPA), triethanolamine (TEA), 1, 2-cyclohexane diamino tetraacetic acid (CDTA), a diethylene triamino 5 methylene phosphoric acid (DTPMP) and 1, 1, 1, 5 and 5, the 5-6 fluoride -2, or 4-2,4-pentanedione.

[0027]

It may be hard to dissolve an above-mentioned organic acid or an above-mentioned chelating agent in a non-polar solvent like a supercritical carbon dioxide. When it is hard to dissolve, even if it mixes an above-mentioned organic acid or an above-mentioned chelating agent directly to a supercritical carbon dioxide, it is difficult to demonstrate the washing engine performance to the heavy-metal-contamination object of an organic acid or a chelating agent.

Then, by adding to supercritical fluid by making a polar organic solvent into a compatible agent, an organic acid or a chelating agent can be stabilized and dissolved in a supercritical carbon dioxide at the pressure and temperature beyond a critical condition, a complexing operation or a chelate effect can be demonstrated, and the

washing engine performance of a supercritical carbon dioxide can be raised.

The addition to the supercritical fluid of a polar organic solvent is 30% or less 10% or more.

[0028]

As such a polar organic solvent, a methanol, ethanol, isopropanol, Alcohols, such as ethylene glycol and a glycerol, an acetone, a methyl ethyl ketone, Lactone, such as ketones, such as methyl isopropyl ketone, and gamma-butyrolactone Nitril, such as ester, such as methyl lactate and ethyl lactate, an acetonitrile, and N-methyl pyrrolidine Ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, A diethylene glycol, the diethylene-glycol monomethyl ether, Diethylene glycol monoethyl ether, the triethylene glycol monomethyl ether, Sulfoxides, such as sulfones, such as ether, such as diethylene-glycol wood ether and dipropylene glycol wood ether, and a sulfolane, and dimethyl sulfoxide, are mentioned. In these, ether, such as the diethylene-glycol monomethyl ether, diethylene glycol monoethyl ether, and dipropylene glycol monomethyl ether, is used especially suitably.

[0029]

Since a washing assistant has critical temperature and the critical pressure higher than a carbon dioxide when using a carbon dioxide as supercritical fluid, in the critical temperature and the critical pressure of an interflow object with a supercritical carbon dioxide, the critical temperature and the critical pressure of a carbon dioxide become high.

Then, it is desirable to hold the temperature and the pressure of a supercritical carbon dioxide highly to 40 degrees C and 10MPa(s), respectively so that a washing assistant may dissolve to a supercritical carbon dioxide well.

the concentration of an organic acid or a chelating agent — 40 degrees C and the supercritical carbon dioxide of 8MPa — less than [more than 0.01mol%2mol%] — it is a density range not more than more than 0.05mol%1mol% preferably. When an organic acid or chelating agent concentration is lower than 0.01-mol%, it is difficult to remove a heavy-metal-contamination object completely, and when higher than two-mol%, an organic acid or a chelating agent does not dissolve into a supercritical carbon dioxide, but there is a possibility of depositing on the washed body.

[0030]

[Embodiment of the Invention]

With reference to an accompanying drawing, the example of an operation gestalt is given to below, and the gestalt of operation of this invention is explained to it at concrete and a detail.

The example 1 of an operation gestalt

This example of an operation gestalt is an example of the operation gestalt of the washing approach concerning the 1st and 2nd invention approaches, and drawing 1 R> 1 is a flow sheet which shows the configuration of washing/dryer used in case the approach of this example of an operation gestalt is enforced.

First, with reference to drawing 1 , the configuration of washing/dryer used in case the approach of this example of an operation gestalt is enforced is explained. Washing / dryer 10 is washing/dryer of the batch type which carries out washing/desiccation processing of the washed body like the wafer which has the low dielectric constant film by which heavy metal pollution was carried out as shown in drawing 5 (c) and drawing 6 (c).

The chamber 16 which washing / dryer 10 has opening 12 in the upper part as shown in drawing 1 , and has the processing room 14 which contains the washed body W by which carrying-in appearance is carried out through opening 12 inside, The lid 18 which seals opening 12, and the fluid source of supply 20 which supplies a processing fluid to the processing room 14, A fluid supply means to introduce a processing fluid in the processing room 14 from the fluid source of supply 20, It has a washing assistant supply means to add a washing assistant in a processing fluid from the washing assistant source of supply 22, a polar organic solvent supply means to add a polar organic solvent in a processing fluid from the polar organic solvent source of supply 24, and a fluid discharge means to discharge the processing fluid with which processing of the washed body was presented from the processing room 14.

[0031]

A processing fluid means the supercritical fluid used as a penetrant remover which removes the heavy-metal-contamination object of the washed body W. Moreover, a washing assistant means an organic acid or a chelating agent. In addition, the supercritical fluid which added the washing assistant may be called processing fluid.

In this example of an operation gestalt, a supercritical carbon dioxide is used as supercritical fluid.

[0032]

Carrying-in appearance of the washed body W is carried out to the processing room 14 through opening 12. Between the opening edge of the opening 12 of the processing room 14, and the lid 18, O ring 26 is arranged as a seal member so that opening 12 can be sealed with a lid 18. With the bolting implements 28, such as ****, a lid 18 is connected with the processing room 14, and seals the processing room 14. That is, the interior of the processing room 14 can be changed into the condition of having been

sealed completely, by binding the lid 18 through O ring 26 tight, and binding tight with an ingredient 28.

Moreover, inside the processing room 14, the washed body maintenance cassette 30 for laying and holding two or more washed bodies W can be arranged.

[0033]

A fluid supply means consists of the pressure and a temperature control means 32 to control a processing fluid to a predetermined pressure and predetermined temperature, a cross valve 34, and a fluid supply port 36 arranged in the processing room 14, and introduces the processing fluid controlled by the pressure and the temperature control means 32 by a predetermined pressure and temperature through the cross valve 34 and the fluid supply port 36 from the fluid source of supply 20 in the processing room 14.

The pressure and the temperature control means 32 consist of [temperature] in-line heaters which carry out a temperature up in the booster pump and processing fluid which carry out the pressure up of the processing fluid.

[0034]

The washing assistant supply means 38 is equipped with a pump etc., and supplies a washing assistant to a processing fluid by the supply line 42 through the closing motion valve 40 from the washing assistant source of supply 22.

The polar organic solvent supply means 44 is equipped with a pump etc., and supplies a polar organic solvent to a processing fluid by the supply line 40 through the closing motion valve 46 from the polar-solvents source of supply 24.

It connects with the cross valve 34 equipped with the feed hopper 48, and a supply line 42 adds the polar organic solvent or washing assistant of the specified quantity in a processing fluid through the fluid supply port 36 by opening adjustment of a cross valve 34.

[0035]

The fluid discharge means consists of a fluid discharge port 50 established in the processing room 14, an exhaust-gas-pressure valve 52, and an effluent liquor decollator 54 connected to the fluid discharge port 50 through the exhaust-gas-pressure valve 52.

[0036]

The exhaust-gas-pressure valve 52 will be opened if the internal pressure of the processing room 14 becomes more than a setting pressure, and it has the function which discharges the processing fluid introduced in the processing room 14. That is, the exhaust-gas-pressure valve 52 can maintain the pressure in the processing room 14 at a predetermined pressure.

The effluent liquor decollator 54 is vapor-liquid-separation equipment, and the

discharged supercritical carbon dioxide (a washing assistant is included) is divided into a gas component and a liquid component by reducing a pressure to atmospheric pressure. A supercritical carbon dioxide evaporates a gas component and it is recovered by the gas recovery system (not shown) as exhaust gas. A washing assistant etc. is separated as a liquid and liquid components are collected as effluent liquor.

The collected exhaust gas is a carbon dioxide etc. and can also be reused. Moreover, the collected effluent liquor is reusable similarly.

[0037]

Furthermore, the side attachment wall of a chamber 16 is equipped with a heating means 56 to heat the processing fluid introduced in the processing room 14, and to hold to predetermined temperature.

The heating means 56 is equipped with the temperature controller 58 which consists of heating media like heating wire, controls the power supplied to heating wire from the power source (not shown) prepared in the exterior of the processing room 14, and controls the temperature of the heating means 56 to predetermined temperature.

[0038]

Although this washing / dryer 10 is equipment which washes two or more washed bodies W by the batch type, washing/dryer of single-wafer-processing processing are also the same configuration as this washing / dryer 10, and a process flow fundamentally, and although it ends with a small processing room, a throughput falls.

[0039]

Next, how to follow the approach of this example of an operation gestalt using above-mentioned washing / dryer 10, and wash / dry the washed body W is explained.

In this example of an operation gestalt, as the washed body W shows drawing 5 (c) or drawing 6 (c), it is the wafer which has the laminated structure by which heavy metal contamination was carried out, and a methanol is used as an organic acid, for example, a citric acid, and a polar organic solvent as a washing assistant.

[0040]

First, the washed body maintenance cassette 30 which held two or more washed bodies W from the opening 12 of the processing room 14 is contained in the processing room 14. Then, a lid 18 is shut, the processing room 14 is changed into a sealing condition, and a supercritical carbon dioxide is introduced in the processing room 14 from the processing fluid source of supply 20.

[0041]

If 7.38 or more MPas are pressurized and a carbon dioxide is heated at 31.1 degrees C or more on the occasion of installation, since it will be in a supercritical condition, the

pressure up of the pressure is preferably carried out for a carbon dioxide to 10MPa(s) with a pressure and the temperature control means 32 from the processing fluid source of supply 20 at 7.38 or more MPas, the temperature up of the temperature is preferably carried out to 40 degrees C, and it is introduced into 31.1 degrees C or more in the processing room 14 through a supply port 36.

To coincidence, the supercritical carbon dioxide introduced in the processing room 14 by the heating means 56 is heated, and the temperature of the supercritical carbon dioxide in the processing room 14 is maintained at 40 degrees C with a temperature controller 58 at it.

A supercritical carbon dioxide is maintained to the temperature of 40 degrees C, and the pressure of 10MPa for raising the solubility of a washing assistant and raising the washing engine performance of a supercritical carbon dioxide.

[0042]

With installation of a supercritical carbon dioxide, opening of the opening of a cross valve 34 is adjusted and carried out, and a washing assistant is added from the washing assistant source of supply 22 with a predetermined appending rate to a supercritical carbon dioxide through a feed hopper 48. In this example of an operation gestalt, an appending rate is 1 % of the weight.

[0043]

A temperature controller 58 performs temperature control of a supercritical carbon dioxide. If the internal pressure of the processing room 14 becomes more than a constant pressure, the exhaust-gas-pressure valve 52 will open and a supercritical carbon dioxide and a washing assistant will be discharged out of a system via the effluent liquor decollator 54.

Thus, it is possible to keep constant the pressure in the processing room 14 and temperature by discharging suitably the supercritical carbon dioxide with which it filled up in the processing room 14.

the supercritical carbon dioxide which added the washing assistant — the washed body W — predetermined time — for example, it is immersed for 10 minutes and a heavy-metal-contamination object is removed. Subsequently, while the washed body W had been made immersed in the supercritical carbon dioxide which added the washing assistant, the closing motion valve 40 is stopped, supply of a washing assistant is suspended, only a supercritical carbon dioxide is supplied to the processing room 14 as a rinse, and a washing assistant is discharged, thinning washing assistant concentration gradually. It is separated by the effluent liquor decollator 54 and recovery playback of the mixed waste fluid of a carbon dioxide and a washing assistant is carried out if

needed.

[0044]

Then, the pressure of the processing room 14 is lowered, and if a carbon dioxide is discharged and it cools, the washed body W will be fulfilled by the gaseous carbon dioxide, and will be dried. In supercritical drying, a pressure is decompressed to atmospheric pressure, holding temperature at 31.1 degrees C or more, after holding temperature at 40 degrees C, holding a pressure to 10MPa(s) and washing, when a carbon dioxide is used, for example as supercritical fluid. Then, temperature is lowered from 31.1 degrees C or more to a room temperature, for example, 20 degrees C.

By this, the washed body W in the processing room 14 will be in dryness. Thus, it becomes possible to make it dry, without destroying the fine structure of the washed body W which has the fine structure like the hole of the porosity low dielectric constant film by passing through supercritical drying.

By passing through the above process, the heavy-metal-contamination object adhering to the washed body W can be removed, and the pure washed body W can be acquired.

[0045]

The example 1 of an experiment

Cu atoms are 1013 atom/cm² before washing as an example 1 of an experiment. When washing/desiccation processing of the wafer which has the laminated structure shown in drawing 6 (c) which was carrying out extent adhesion is carried out by the approach of this example of an operation gestalt, as it is shown in drawing 2, it is the coating weight of Cu atom of a wafer 1010 atom/cm². It could decrease to extent and sufficient heavy-metal-contamination removal was able to be attained.

When a washing assistant was not added but washing/desiccation processing of the same wafer as the example 1 of an experiment was carried out by using only a supercritical carbon dioxide as a processing fluid as an example of a comparison, the coating weight of Cu atom of a wafer is 1012 atom/cm². It is extent and the coating weight of Cu atom was almost changeless washing before.

[0046]

The example 2 of an experiment

Moreover, it is after washing, the structure before wiring layer membrane formation (presentation) was investigated using infrared absorption spectrometry, and the presentation change before and behind washing was indicated to be the structure before washing of the porosity low dielectric constant film when washing the porosity low dielectric constant film before wiring layer membrane formation by the washing approach of the example 1 of an operation gestalt (presentation) shown in drawing 6 (a)

to drawing 3 .

The wave number (cm⁻¹) of an infrared absorption spectrum is taken along a horizontal axis, it takes an absorbance (arbitration graduation) along an axis of ordinate, and drawing 3 shows the graph which shows the relation between the wave number (cm⁻¹) of the infrared absorption spectrum before washing on the upper case, and an absorbance, and the graph which shows the relation between the wave number (cm⁻¹) of the infrared absorption spectrum after washing in the lower berth, and an absorbance. In addition, although the absorbance before and behind washing is the same, in order to show the location of the peak wave number clearly, it dissociates up and down and it is displayed.

[0047]

Si-O, Si-H, Si-OH, Si-CH₃ which are before and after washing and constitute the porosity low dielectric constant film so that drawing 3 may show Change was not looked at by association of C-H etc. Therefore, since are before and after washing and presentation change has not arisen, i.e., it is before and after washing and is changeless in the structure of the low dielectric constant film, it can be judged that that a hole is crushed and a dielectric constant changes has not arisen.

Without it seeming that the porosity low dielectric constant film passes a gas-liquid interface, and the porous hole was crushed on the occasion of washing and desiccation like before since the gas-liquid interface was not generating to a supercritical carbon dioxide so that the examples 1 and 2 of an experiment might show, the heavy-metal-contamination object was removed and it has checked that it could be made to dry.

[0048]

In addition, if the closing motion valve 46 is opened wide and it pours into supercritical fluid via the supply line 42 and the cross valve 34 from the polar organic solvent source of supply 24 with the polar-solvents supply means 44 before pouring a washing assistant into a supercritical carbon dioxide, the solubility of a washing assistant can be raised further. The addition ratio of a polar organic solvent is 20% or less more than per %.

[0049]

Although chemical mechanical polishing (Chemical Mechanical Polishing: CMP) was made into the example and explained as the polish approach of a metal membrane, as the polish approach, it is not restricted only to CMP. For example, the heavy metal contamination generated in electrolytic polishing (Electro Chemical Polishing : ECP) etc. can be similarly removed by the washing approach of this invention, without

changing the structure of the porosity low dielectric constant film.

[0050]

Although the wafer equipped with the wiring structure using the porosity low dielectric constant film formed by the production process of LSI as the washed body is made into the example by the approach of this example of an operation gestalt, it is applicable also like many of microstructures of others which are formed by the production process of LSI.

moreover — when it is the micro machine which has the moving part which consists of Ayr bridge structure and the approach of this example of an operation gestalt was applied by use as the wash body that by which heavy metal contamination was carried out, without the Ayr bridge front face is eat away like before after washing — moreover, the substrate of the Ayr bridge — also stick — it checked that there was nothing and a heavy metal contamination object could be removed.

[0051]

The example 2 of an operation gestalt

Although washing/desiccation processing of the washed body by which is the wafer which embedded on the porosity low dielectric constant film, and prepared wiring, and heavy metal contamination was carried out is carried out in the example 1 of an operation gestalt, this invention approach is applicable also to the washed bodies other than these.

This example of an operation gestalt is an example of an operation gestalt which applied the washing approach concerning the 1st and 2nd invention approaches to weak washing of the electrode structure of structure which has the pattern of a high aspect ratio shown in drawing 4 prepared in the large-scale integrated circuit. It is the sectional view of each process at the time of (c) forming electrode structure from drawing 4 (a), respectively.

In this example of an operation gestalt, as shown in drawing 4 (a), after forming an insulator layer thin as the 1st layer 64 on the Si substrate 62 first, one by one, the 2nd layer (insulator layer) 66, the 3rd layer (metal membrane) 68, and the 4th layer (insulator layer) 70 are formed, and a laminated structure is formed.

The resist film is applied on the 4th layer 70, photolithography processing is performed, and the resist mask 72 is formed.

Then, the 4th layer 70, the 3rd layer 68, and the 2nd layer 64 are etched by the dry etching method from on the resist mask 72, and as shown in drawing 4 (b), the electrode structure 74 of the detailed pattern which consists of the 3rd layer (metal membrane) 68 is formed on the 1st layer 64 of the Si substrate 62.

[0052]

By the way, since the etch residue and the heavy-metal-contamination object have adhered to the side attachment wall of the 2nd layer 64 and the 3rd layer 68 as shown in drawing 4 (b), it is necessary to remove.

Although the residue of an organic component like resist material is removable at a resist removal process, a heavy-metal-contamination object is unremovable. Then, although it is necessary to wash and remove a heavy-metal-contamination object apart from a resist removal process, in washing by the usual penetrant remover, the aspect ratio of a pattern is large and the pattern of the electrode structure 74 collapses.

Then, without collapsing a detailed pattern by using washing / dryer 10, adding an organic acid or a chelating agent as a washing assistant to supercritical fluid, for example, a supercritical carbon dioxide, like the example 1 of an operation gestalt, and carrying out washing processing of the electrode structure 74, as shown in drawing 4 (c), the detailed electrode structure 74 which removed the heavy-metal-contamination object can be formed.

[0053]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the flow sheet which shows the configuration of washing/dryer used in case the approach of the example 1 of an operation gestalt is enforced.

[Drawing 2] Drawing 2 is a bar graph which shows the result of having carried out counting of the number of the heavy-metal contaminations before and behind washing of the washed body in the example 1 of an experiment, and the example of a comparison (particle).

[Drawing 3] The wave number (cm⁻¹) of an infrared absorption spectrum is taken along a horizontal axis, an absorbance (arbitration graduation) is taken along an axis of ordinate, and the graph which shows the relation between the wave number (cm⁻¹) of the infrared absorption spectrum before washing and after washing and an absorbance to an upper case and the lower berth, respectively is shown.

[Drawing 4] It is the sectional view of each process at the time of (c) forming electrode structure from drawing 4 (a), respectively.

[Drawing 5] It is a sectional view explaining each process at the time of the porosity low dielectric constant film being used for (c) from drawing 5 (a), respectively, and forming metal wiring and a metal plug according to a single DAMASHIN process.

[Drawing 6] It is a sectional view explaining each process at the time of the porosity

low dielectric constant film being used for (c) from drawing 6 (a), respectively, and a dual DAMASHIN process explaining metal wiring and a metal plug.

[Description of Notations]

10 [.. Chamber,] Washing/dryer, 12 .. Opening, 14 .. A processing room, 16 18 [.. Polar-solvents source of supply,] A lid, 20 .. A fluid source of supply, 22 .. A washing assistant source of supply, 24 26 An O ring, 28 .. A bolting implement, 30 .. Washed body maintenance cassette, 32 A pressure and a temperature control means, 34 .. A cross valve, 36 .. Fluid supply port, 38 A washing assistant supply means, 40 .. A closing motion valve, 42 .. Supply line, 44 [.. Fluid discharge port,] A polar-solvents supply means, 46 .. A closing motion valve, 48 .. A feed hopper, 50 52 [.. Temperature controller,] An exhaust-gas-pressure valve, 54 .. An effluent liquor decollator, 56 .. A heating means, 58 62 Si substrate, 64 .. The 1st layer (thin insulator layer), 66 .. The 2nd layer (insulator layer), 68 The 3rd layer (metal membrane), 70 .. The 4th layer (insulator layer), 72 .. Resist mask, 74 Electrode structure, 76 .. The substrate film, 78 .. Etching mask layer, 80 The porosity low dielectric constant film, 82 .. A contact hole, 84 .. Wiring gutter, 86 [.. Embedding wiring,] A reaction prevention layer, 88 .. A metal membrane, 90 .. A metal plug, 92 93 A heavy-metal-contamination object, 94 .. The substrate film, 96 .. The 1st porosity low dielectric constant film, 98 The 1st etching mask layer, 100 .. The 2nd porosity low dielectric constant film, 102 [.. A reaction prevention layer, 112 / .. 114 A metal membrane, 116 / .. A metal plug, 118 / .. Embedding wiring, 120 / .. Heavy-metal-contamination object] 104 The 2nd etching mask layer, 106 .. A contact hole, 108 .. A wiring gutter, 110

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【特許請求の範囲】

【請求項 1】

金属汚染されている被洗浄体を超臨界流体で洗浄する方法において、洗浄助剤として有機酸又はキレート剤を所定添加率で添加した超臨界流体を洗浄液として使用し、洗浄助剤を添加した超臨界流体に被洗浄体を接触させて洗浄する洗浄工程を有することを特徴とする洗浄方法。

【請求項 2】

洗浄工程に続いて、超臨界流体をガス化して被洗浄体を乾燥する工程を有することを特徴とする請求項 1 に記載の洗浄方法。

【請求項 3】

洗浄工程に続いて、超臨界流体のみを供給してリンス洗浄を被洗浄体に施すリンス工程と、次いで、超臨界流体をガス化して被洗浄体を乾燥させる工程とを有することを特徴とする請求項 1 に記載の洗浄方法。

【請求項 4】

金属汚染されている被洗浄体を超臨界流体で洗浄する方法において、1 槽の洗浄／乾燥チャンバを有する 1 槽式洗浄／乾燥装置を使用し、被洗浄体を収容する洗浄／乾燥チャンバに、洗浄助剤として有機酸又はキレート剤を所定添加率で超臨界流体に添加して供給し、被洗浄体を洗浄する工程と、次いで、超臨界流体のみを洗浄／乾燥チャンバに供給して洗浄助剤を添加した超臨界流体を超臨界流体で置換しつつ被洗浄体をリンス洗浄する工程と、次いで、超臨界流体をガス化して除去し、被洗浄体を乾燥させる工程とを有し、1 槽の洗浄／乾燥チャンバ内で洗浄処理及び乾燥処理を順次行うことを特徴とする洗浄方法。

【請求項 5】

超臨界流体として超臨界二酸化炭素を使用することを特徴とする請求項 1 から 4 のいずれか 1 項に記載の洗浄方法。

【請求項 6】

極性有機溶剤を超臨界二酸化炭素に溶解させ、次いで洗浄助剤溶液を超臨界二酸化炭素に注入することを特徴とする請求項 5 に記載の洗浄方法。

【請求項 7】

有機酸として、クエン酸、リンゴ酸のいずれかを用いることを特徴とする請求項 1 から 6 のうちのいずれか 1 項に記載の洗浄方法。

【請求項 8】

キレート剤として、ジエチレントリアミン五酢酸 (DTPA)、トリエタノールアミン (TEA)、1, 2-シクロヘキサンジアミノ四酢酸 (CDTA)、ジエチレントリアミノ五メチレンリン酸 (DTPMP)、及び 1, 1, 1, 5, 5, 5-六フッ化-2, 4-ペンタンジオンのいずれかを用いることを特徴とする請求項 1 から 7 のうちのいずれか 1 項に記載の洗浄方法。

【発明の詳細な説明】

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【0001】

【発明の属する技術分野】

本発明は、洗浄方法に関し、更に詳しくは、タングステン、アルミニウム、銅等の金属で汚染された被洗浄体、特に CMP や ECP を適用して形成した埋め込み配線を有するウエハの洗浄に最適な洗浄方法に関するものである。

【0002】

【従来の技術】

トランジスタ等の半導体装置の金属配線を形成する工程では、従来、金属配線形成用の金属膜を成膜した後、金属膜上にレジスト膜を成膜し、レジスト膜をパターニングしてエッチングマスクを形成する。続いて、エッチングマスク上から金属膜をドライエッチング法によりエッチングして金属配線を形成している。

また、半導体装置の配線構造で上下配線を接続する金属プラグを形成する工程では、コンタクトホールを形成した絶縁膜上に金属プラグ形成用の金属膜を成膜してコンタクトホールを埋め込んだ後、金属膜全面をエッチバックして金属プラグを形成している。

【0003】

ところで、近年、デバイスの高集積化、高アスペクト化などが進むにつれて、0.18 ミクロンデバイス世代以降では、埋め込み金属配線及び金属プラグの形成に際し、絶縁膜上の金属膜を研磨して除去する際、化学的機械研磨 (Chemical Mechanical Polishing : CMP) や、電解研磨 (Electro Chemical Polishing : ECP) を適用するようになって来ている。

【0004】

例えば、半導体装置の配線形成では、CMP や ECP により絶縁膜上の金属層を研磨、除去して埋め込み金属配線を形成する、いわゆるダマシンプロセスが使用されている。

ダマシンプロセスでは、まず、反応性イオンエッチング (RIE) 法等によりウエハ上の SiO_2 等の層間絶縁層をエッチングして配線溝を形成する。次いで、例えばアルミニウム膜や銅膜などの金属膜をウエハの全面に CVD 法やスパッタ法またはめっき法により成膜して配線溝を埋め込み、続いて CMP や ECP によって層間絶縁層上の金属膜を研磨して除去し、配線溝内に埋め込み金属配線を形成している。

【0005】

また、金属プラグの形成でも、同じく CMP を適用している。まず、 SiO_2 等の層間絶縁層に反応性イオンエッチング (RIE) 法等により接続孔を形成する。次いで、スパッタ法又は CVD 法により密着層として例えばチタン膜、窒化チタン膜、窒化タンタル膜等を接続孔の孔壁を含めてウエハ全面に成膜し、続いて CVD 法により例えばタングステン膜を密着層上に成膜して接続孔

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を埋め込む。次いで、CMPにより、層間絶縁層上のタングステン膜及び密着層を研磨して、金属プラグを接続孔内に形成する。

【0006】

ところで、従来の金属膜のCMP法では、回転する研磨板（プラテンとも言う）上にウエハを載置し、スラリー状の研磨剤を用いてウエハ上の金属膜を研磨した後、金属膜の研磨面を洗浄しているため、以下のような問題があった。

第1には、研磨剤スラリーに由来する金属酸化物やセラミックなどからなる大量のパーティクルがウエハ表面に残留すること、及びウエハ表面に傷（スクラッチ）が発生し易いということである。

第2には、研磨剤スラリーに含まれる金属酸化物によりウエハ表面が金属汚染されるという懸念である。特に、重金属汚染が層間絶縁膜上または層間絶縁膜中に発生すると、配線間リークを引き起こしてしまうので、極めて重大な問題となる。

ECMPにより層間絶縁膜上の金属膜を研磨した場合にも、同様の重金属汚染が問題となる。

【0007】

一方、LSIの高速化のためには、配線間容量を低下させることが不可欠である。そこで、配線間容量を低下させるために、配線間の層間絶縁膜として低誘電率膜が用いられるようになっている。

更に一層低誘電率の層間絶縁膜を成膜するために、膜材料の選定だけでなく、層間絶縁膜の膜質を多孔質にする試みが成されている。

【0008】

ここで、図5を参照して、層間絶縁膜として多孔質低誘電率膜を使い、シングルダマシンプロセスにより埋め込み金属配線及び金属プラグを形成する方法を説明する。

図5(a)から(c)は、多孔質低誘電率膜を使い、シングルダマシンプロセスにより金属配線及び金属プラグを形成する際の各工程を説明する断面図である。

まず、図5(a)に示すように、エッチングマスク層78を介して下地膜76上に多孔質低誘電率膜80を成膜し、次いで低誘電率膜80に下地膜76に達するコンタクトホール82及び配線溝84を形成する。

次いで、図5(b)に示すように、コンタクトホール82及び配線溝84の壁に反応防止層86を成膜し、続いて金属プラグ形成用の金属膜88を低誘電率膜80上に成膜し、コンタクトホール82及び配線溝84を埋め込む。

次いで、図5(c)に示すように、CMPを施して金属膜88を研磨して、低誘電率膜80を露出させると共に金属プラグ90及び埋め込み配線92を形成する。

【0009】

ところで、CMP後には、図5(c)に示すように、金属膜残渣やCMPの研磨剤スラリーから生じる重金属汚

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染物93が、低誘電率膜80上または低誘電率膜80中に発生する。

低誘電率膜80がこれらの重金属汚染物93により金属汚染されたままで製品化すると、配線間リーク等が発生するので、重金属汚染物93を除去し、低誘電率膜80を清浄化することが必要である。

【0010】

また、デュアルダマシンプロセスにより埋め込み配線を形成する際には、図6(a)に示すように、下地膜94上に、順次、第1多孔質低誘電率膜96、第1エッチングマスク層98、第2多孔質低誘電率膜100、及び第2エッチングマスク層102を成膜する。続いて、第1エッチングマスク層98及び第2エッチングマスク層102から形成したエッチングマスクを使って、下地膜94に達するコンタクトホール104、コンタクトホール106、及び配線溝108を形成する。次いで、コンタクトホール104、106及び配線溝108の壁に反応防止層110を成膜する。

図6(b)に示すように、配線及び金属プラグ形成用の金属膜112を第2エッチングマスク層102上に成膜し、コンタクトホール104、106及び配線溝108を埋め込む。

次いで、図6(c)に示すように、CMPを金属膜112及び第2エッチングマスク層102に施して研磨し、第2多孔質低誘電率膜100を露出させると共に、金属プラグ114、116及び埋め込み配線118を形成する。

【0011】

ところで、CMP後には、図6(c)に示すように、金属膜残渣や研磨剤スラリーから生じる重金属汚染物120が、第2多孔質低誘電率膜100上または膜中に発生する。

これらの重金属汚染物により金属汚染されたままで製品化すると、配線間リーク等が発生するので、重金属汚染物を除去し、第2多孔質低誘電率膜100を清浄化することが必要である。

尚、図6(a)から(c)は、それぞれ、多孔質低誘電率膜を使い、デュアルダマシンプロセスにより金属配線及び金属プラグを形成する際の各工程を説明する断面図である。

【0012】

以上述べたように、配線間リーク等の生じないLSIデバイスを製造するためには、これら重金属汚染物を除去しなければならないが、その際に、次のような解決すべき問題があった。

通常、重金属を除去する場合には、洗浄水として水を使った湿式洗浄を施し、次いで乾燥を行っている。しかし、洗浄に際し、表面張力が大きい水などの洗浄液が多孔質低誘電率膜の孔に出入りするとき、洗浄液の圧力と大気圧との圧力差が気液界面に発生するために、多孔質低

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誘電率膜の孔が潰れてしまい、膜質が変化して低誘電率膜の誘電率が高くなってしまうことが多い。これでは、多孔質低誘電率膜を使用する効果が減退する。

【0013】

孔が潰れないようにするために、表面張力の小さな流体を用いて洗浄／乾燥すれば良い。

例えば、水の表面張力は約 72 dyn/cm であるが、メタノールの表面張力は約 23 dyn/cm であるから、水洗浄した後に直ちに乾燥させるよりも、水洗浄した後、水をメタノールで置換し、次いで乾燥させる方が、
10 低誘電率膜の膜質の変化を抑え易い。

しかし、メタノールの表面張力も無視できるほど小さくないので、大なり小なり孔が潰れる。従って、膜質の変化を完全に防止することができず、完全な問題解決とはならない。

【0014】

多孔質低誘電率膜の孔が潰れるようなことが無いようにするためには、リンス液として表面張力がゼロである流体を使って洗浄するか、そのような液体でリンスした後、乾燥させるか、又は表面張力がゼロの流体でリンス液
20 を置換した後、乾燥することである。

表面張力がゼロの流体として、超臨界流体を挙げることができる。超臨界状態とは、物質に固有の臨界温度および臨界圧力下で物質がとる状態相の一つであり、超臨界流体とは超臨界状態にある流体を言う。

超臨界流体は、他の液体や固体に対する溶解力が液体状態の流体とほぼ同等である一方、その粘度が著しく小さく、拡散係数が極めて大きいという特異な性質を有している。換言すれば、気体の特性を持った液体と言える。従って、超臨界流体は、気液界面を形成しないので、表面張力がゼロになる。そこで、超臨界状態で被洗浄体を乾燥すれば、表面張力が存在しないので、気液界面の発生による圧力差は全く生じないことになる。
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【0015】

超臨界流体は圧力が臨界圧力以下になると速やかにガス化するので、超臨界流体を使って洗浄した後、減圧することにより、容易に超臨界流体を放出することができる。

従って、多孔質低誘電率膜が表面に露出している基板を洗浄した後、洗浄液から直接に、又は洗浄液で洗浄し、
40 次いでリンス液でリンスした後に、或いはリンスした後、リンス液を別の液体で置換した後に、洗浄液、リンス液、或いは別の液体が付着している基板を耐圧容器内の超臨界流体に接触させ、これらの液体を超臨界流体に溶解させることにより、基板に付着した液体を容易に除去することができる。

次いで、耐圧容器内の温度を臨界温度以上に保ったまま耐圧容器内の圧力を臨界圧力以下に減じて超臨界流体をガス化することにより、耐圧容器から基板を大気中に取り出すことができる。

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超臨界流体の表面張力は極めて小さいので、超臨界流体が基板表面から除去される際にその表面張力によりウエハの微小構造、例えばパターンや多孔質低誘電率膜の孔に与える応力は無視し得る程度である。従って、多孔質低誘電率膜に変質が生じるようなことはない（特開 2000-154273 号公報）。

【0016】

超臨界流体として、二酸化炭素、アンモニア、水、アルコール類、低分子量の脂肪族飽和炭化水素類、ベンゼン、ジエチルエーテルなどの超臨界状態となることが確認されている多くの物質を利用することができる。

これらの物質の中で、超臨界温度が 31.3°C と室温に近い二酸化炭素は、取り扱いが容易であること、及び被洗浄体を高温に曝すことなく洗浄／乾燥できるという理由から、洗浄液として好ましい物質の一つである。

【0017】

【特許文献 1】

特開平 10-135170 号公報（図 1）

【特許文献 2】

特許第 2574781 号公報（図 1）

【0018】

【発明が解決しようとする課題】

しかし、超臨界二酸化炭素による従来の洗浄方法には、以下のような問題があった。

第 1 には、超臨界二酸化炭素の溶解性は無極性有機溶剤のような性質であるために、超臨界二酸化炭素単体の溶解性能には選択性がある。そのために、低分子の有機物の溶解除去、油脂やワックスなどの溶解除去は可能であるが、イオン性の金属や金属酸化物等の金属汚染物の除去には洗浄効果が低いという問題である。

第 2 には、重金属汚染物をリフトオフにより除去するために、超臨界二酸化炭素にエッチング力を有する化学物質や酸化力を有する化学物質を添加した場合、多孔質低誘電率膜の膜構造がエッチングないし酸化されて変化してしまい、誘電率が高くなるという問題である。また、多孔質低誘電率膜内に形成された埋め込み配線もエッチングされ、配線抵抗が増加して、配線遅延を引き起こすという問題もある。

このように、従来の超臨界二酸化炭素による洗浄方法では、多孔質低誘電率膜の膜質を変化させることなく、また膜質・膜構造を保持したまま、重金属汚染物を確実に除去することが難しかった。

【0019】

そこで、本発明の目的は、被洗浄体に損傷を与えることなく、金属汚染された被洗浄体を洗浄して浄化する洗浄方法を提供することであって、例えば被洗浄体が多孔質低誘電率膜内に埋め込み配線を有するものである場合、多孔質低誘電率膜の膜質、膜構造等を変化させることなく、また多孔質低誘電率膜内に形成された埋め込み配線に損傷を与えることなく、金属汚染された被洗浄体を洗
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浄、浄化することである。

【0020】

【課題を解決するための手段】

本発明者は、上記目的を解決するために研究を続けた過程で、CMP後の多孔質低誘電率膜等の金属汚染された被洗浄体を超臨界二酸化炭素により洗浄する際に、予め洗浄助剤として有機酸又はキレート剤を超臨界流体、例えば超臨界二酸化炭素に微量添加し、それを洗浄液として使って被洗浄体を洗浄処理することにより、重金属汚染物を確実に洗浄、除去し、かつ被洗浄体を乾燥すること

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【0021】

超臨界流体は、微細部への浸透性が液体より高いので、多孔質低誘電率膜の孔等の微細構造体と重金属汚染物との間へ有機酸またはキレート剤を同伴することが容易であって、これにより重金属汚染物を捕捉、除去させることができる。また、超臨界流体は、密度が気体より高いので、除去された重金属汚染物を容易に取り去り、洗

流することができる。洗浄助剤を用いているので、エッチング作用を有する化学物質を添加する必要がなく、従来のように、配線金属材料が侵食されて、配線抵抗が増加するようなことが生

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【0022】

上記目的を達成するために、上述の知見に基づいて、本発明に係る洗浄方法（以下、第1の発明方法と言う）は、金属汚染されている被洗浄体を超臨界流体で洗浄する方法において、洗浄助剤として有機酸又はキレート剤を所定添加率で添加した超臨界流体を洗浄液として使用し、洗浄助剤を添加した超臨界流体に被洗浄体を接触させて洗浄する洗浄工程を有することを特徴としている。

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【0023】

本発明方法の好適な実施態様では、洗浄工程に続いて、超臨界流体をガス化して被洗浄体を乾燥する工程を有する。

また、本発明方法の好適な別の実施態様では、洗浄工程に続いて、超臨界流体のみを供給してリンス洗浄を被洗浄体に施すリンス工程と、次いで、超臨界流体をガス化して被洗浄体を乾燥する工程とを有する。

【0024】

1槽の洗浄／乾燥チャンバを有する1槽式洗浄／乾燥装置を使用する本発明に係る洗浄方法（以下、第2の発明方法と言う）は、金属汚染されている被洗浄体を超臨界流体で洗浄する方法において、1槽の洗浄／乾燥チャンバを有する1槽式洗浄／乾燥装置を使用し、被洗浄体を収容する洗浄／乾燥チャンバに、洗浄助剤として有機酸又はキレート剤を所定添加率で超臨界流体に添加して供給し、被洗浄体を洗浄する工程と、次いで、超臨界流体のみを洗浄／乾燥チャンバに供給して洗浄助剤を添加した超臨界流体を超臨界流体で置換しつつ被洗浄体をリン

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そこで、極性有機溶剤を相溶剤として超臨界流体に添加することにより、臨界条件以上の圧力および温度で、有機酸またはキレート剤を超臨界二酸化炭素に安定して溶解させることができ、錯化作用またはキレート作用を発揮させ、超臨界二酸化炭素の洗浄性能を向上させることができる。

極性有機溶剤の超臨界流体に対する添加量は10%以上30%以下である。

【0028】

このような極性有機溶剤としては、メタノール、エタノール、イソプロパノール、エチレングリコール、グリセ

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ス洗浄する工程と、次いで、超臨界流体をガス化して除去し、被洗浄体を乾燥させる工程とを有し、1槽の洗浄／乾燥チャンバ内で洗浄処理及び乾燥処理を順次行うことを特徴としている。

【0025】

洗浄助剤として使用できる有機酸またはキレート剤の条件は、超臨界二酸化炭素等の超臨界流体に良好に溶解し、超臨界流体の臨界条件以上の圧力および温度下で安定であることである。

第1及び第2の発明方法で洗浄助剤として使用できる有機酸として、シュウ酸、マロン酸、クエン酸、コハク酸、リンゴ酸などがあるが、特に重金属汚染物を安定して確実に捕捉する有機酸としてクエン酸及びリンゴ酸が好ましい。

【0026】

また、第1及び第2の発明方法で使用できるキレート剤としては、エチレンジアミン四酢酸（EDTA）、ジエチレントリアミン五酢酸（DTPA）、トランス-シクロヘキサ-1,2-ジアミン四酢酸（CyDTA）、ニトリロ三酢酸（NTA）、イミノ二酢酸（IDA）、トリエタノールアミン（TEA）、1,2-シクロヘキサジアミノ四酢酸（CDTA）、ジエチレントリアミノ五メチレンリン酸（DTPMP）、ヒドロキシエチルニリン酸（HEDP）、アセチルアセトン誘導体、1,1,1,5,5,5-六フッ化-2,4-ペンタンジオンなどである。

特に、重金属汚染物を安定して確実に捕捉するキレート剤は、ジエチレントリアミン五酢酸（DTPA）、トリエタノールアミン（TEA）、1,2-シクロヘキサジアミノ四酢酸（CDTA）、ジエチレントリアミノ五メチレンリン酸（DTPMP）、及び1,1,1,5,5,5-六フッ化-2,4-ペンタンジオンのいずれかである。

【0027】

上述の有機酸またはキレート剤は、超臨界二酸化炭素のような無極性溶媒には溶解し難いこともある。溶解し難いと、上述の有機酸またはキレート剤を超臨界二酸化炭素に直接混合しても、有機酸またはキレート剤の重金属汚染物に対する洗浄性能を発揮させることが難しい。

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リン等のアルコール類、アセトン、メチルエチルケトン、メチルイソプロピルケトン等のケトン類、 γ -ブチロラクトン等のラクトン類、乳酸メチル、乳酸エチル等のエステル類、アセトニトリル、N-メチルピロリジン等のニトリル類、エチレングリコールモノメチルエーテル、エチレングリコールモノエチルエーテル、ジエチレングリコール、ジエチレングリコールモノメチルエーテル、ジエチレングリコールモノエチルエーテル、トリエチレングリコールモノメチルエーテル、ジエチレングリコールジメチルエーテル、ジプロピレングリコールジメチルエーテル等のエーテル類、スルホラン等のスルホン類、ジメチルスルホキシド等のスルホキシド類等が挙げられる。これらの中で、ジエチレングリコールモノメチルエーテル、ジエチレングリコールモノエチルエーテル、ジプロピレングリコールモノメチルエーテルなどのエーテル類が特に好適に使用される。

【0029】

超臨界流体として二酸化炭素を用いるときには、洗浄剤は、二酸化炭素より臨界温度および臨界圧力が高いので、超臨界二酸化炭素との混合流体の臨界温度および臨界圧力は、二酸化炭素の臨界温度および臨界圧力は高くなる。

そこで、洗浄剤が超臨界二酸化炭素に良く溶解するように、超臨界二酸化炭素の温度及び圧力を、それぞれ、例えば40℃及び10MPaに高く保持することが望ましい。

有機酸またはキレート剤の濃度は、例えば40℃、8MPaの超臨界二酸化炭素では0.01mol%以上2mol%以下、好ましくは0.05mol%以上1mol%以下の濃度範囲である。有機酸またはキレート剤濃度が0.01mol%より低いときには、重金属汚染物を完全に除去することが難しく、2mol%よりも高いときには、有機酸またはキレート剤が超臨界二酸化炭素中に溶解せず、被洗浄体上に析出するおそれがある。

【0030】

【発明の実施の形態】

以下に、添付図面を参照し、実施形態例を挙げて本発明の実施の形態を具体的かつ詳細に説明する。

実施形態例1

本実施形態例は、第1及び第2の発明方法に係る洗浄方法の実施形態の一例であって、図1は本実施形態例の方法を実施する際に使用する洗浄／乾燥装置の構成を示すフローシートである。

先ず、図1を参照して、本実施形態例の方法を実施する際に使用する洗浄／乾燥装置の構成を説明する。洗浄／乾燥装置10は、図5(c)及び図6(c)に示したような重金属汚染された低誘電率膜を有するウエハのような被洗浄体を洗浄／乾燥処理するバッチ式の洗浄／乾燥装置である。

洗浄／乾燥装置10は、図1に示すように、上部に開口

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部12を有し、開口部12を介して搬入出される被洗浄体Wを収納する処理室14を内部に有するチャンバ16と、開口部12を密閉する蓋18と、処理室14に処理流体を供給する流体供給源20と、流体供給源20から処理流体を処理室14内に導入する流体供給手段と、洗浄剤供給源22から洗浄剤を処理流体に添加する洗浄剤供給手段と、極性有機溶剤供給源24から極性有機溶剤を処理流体に添加する極性有機溶剤供給手段と、被洗浄体の処理に供された処理流体を処理室14から排出する流体排出手段とを備えている。

【0031】

処理流体とは、被洗浄体Wの重金属汚染物を除去する洗浄液として使用される超臨界流体を言う。また、洗浄剤とは、有機酸若しくはキレート剤を言う。尚、洗浄剤を添加した超臨界流体を処理流体と言うこともある。本実施形態例では、超臨界流体として超臨界二酸化炭素を使用する。

【0032】

被洗浄体Wは、開口部12を介して処理室14に搬入出される。開口部12を蓋18で密閉できるように、処理室14の開口部12の開口縁と蓋18との間には、シール部材としてOリング26が配されている。蓋18は、ねじ等の締め付け具28によって処理室14に連結され、処理室14を密閉する。つまり、Oリング26を介した蓋18を締め付け具28で締め付けることにより、処理室14の内部を完全に密閉された状態にすることができる。

また、処理室14の内部には、複数個の被洗浄体Wを載置、保持するための被洗浄体保持力セット30を配置することができる。

【0033】

流体供給手段は、処理流体を所定の圧力及び所定の温度に制御する圧力・温度制御手段32と、三方弁34と、処理室14に配設された流体供給ポート36とで構成され、流体供給源20から三方弁34及び流体供給ポート36を介し、圧力・温度制御手段32によって所定の圧力及び温度に制御された処理流体を処理室14内に導入する。

圧力・温度制御手段32は、処理流体を昇圧する昇圧ポンプ及び処理流体を温度を昇温するインラインヒータ等から構成されている。

【0034】

洗浄剤供給手段38は、ポンプ等を備え、洗浄剤供給源22から開閉弁40を介して供給ライン42により処理流体に洗浄剤を供給する。

極性有機溶剤供給手段44は、ポンプ等を備え、極性有機溶剤供給源24から開閉弁46を介して極性有機溶剤を供給ライン40により処理流体に供給する。

供給ライン42は、供給口48を備えた三方弁34に接続され、三方弁34の開度調整により、流体供給ポート

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36を介して処理流体に所定量の極性有機溶剤又は洗浄助剤を添加する。

【0035】

流体排出手段は、処理室14に設けられた流体排出ポート50と、排圧弁52と、排圧弁52を介して流体排出ポート50に接続された排出液分離装置54とから構成されている。

【0036】

排圧弁52は、処理室14の内部圧力が設定圧力以上になると開き、処理室14内に導入された処理流体を排出する機能を有する。つまり、排圧弁52によって、処理室14内の圧力を所定圧力に保つことができる。

排出液分離装置54は、気液分離装置であって、圧力を大気圧に低下させることにより、排出された超臨界二酸化炭素（洗浄助剤を含む）を気体成分と液体成分に分離する。気体成分は超臨界二酸化炭素が気化したものであって、排ガスとして気体回収装置（図示せず）により回収される。液体成分は、洗浄助剤等が液体として分離されたものであって、排出液として回収される。

回収された排気ガスは二酸化炭素等であって、再利用することもできる。また、回収された排出液も同様に再利用できる。

【0037】

更に、チャンバ16の側壁には、処理室14内に導入された処理流体を加熱して所定の温度に保持する加熱手段56が備えられている。

加熱手段56は、電熱線のような加熱媒体で構成され、処理室14の外部に設けられた電源（図示せず）から電熱線に供給する電力を制御して、加熱手段56の温度を所定の温度に制御する温度制御装置58を備えている。

【0038】

本洗浄／乾燥装置10は、複数個の被洗浄体Wをバッチ式で洗浄する装置であるが、枚葉式処理の洗浄／乾燥装置も、基本的には本洗浄／乾燥装置10と同様の構成とプロセスフローであって、小さな処理室で済むもののスループットが低下する。

【0039】

次に、上述の洗浄／乾燥装置10を使って本実施形態例の方法に従って被洗浄体Wを洗浄／乾燥する方法を説明する。

本実施形態例では、被洗浄体Wが図5（c）又は図6（c）に示すように重金属汚染された積層構造を有するウエハであって、洗浄助剤として有機酸、例えばクエン酸、極性有機溶媒として例えばメタノールを使用する。

【0040】

まず、処理室14の開口部12から複数個の被洗浄体Wを保持した被洗浄体保持カセット30を処理室14内に収納する。続いて、蓋18を閉めて処理室14を密閉状態にし、処理流体供給源20から超臨界二酸化炭素を処理室14内に導入する。

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【0041】

導入に際して、二酸化炭素を7.38MPa以上に加圧し、31.1℃以上に加熱すると、超臨界状態となるので、処理流体供給源20から二酸化炭素を圧力・温度制御手段32により圧力を7.38MPa以上に、好ましくは10MPaに昇圧し、温度を31.1℃以上に、好ましくは40℃に昇温して供給ポート36を介して処理室14内に導入する。

同時に、加熱手段56によって処理室14内に導入された超臨界二酸化炭素を加熱し、温度制御装置58により処理室14内の超臨界二酸化炭素の温度を40℃に維持する。

超臨界二酸化炭素を40℃の温度、10MPaの圧力に維持するのは、洗浄助剤の溶解度を高めて、超臨界二酸化炭素の洗浄性能を高めるためである。

【0042】

超臨界二酸化炭素の導入と共に、三方弁34の開度を調節して開口し、洗浄助剤を洗浄助剤供給源22から供給口48を介して超臨界二酸化炭素に所定の添加率で添加する。本実施形態例では、添加率は1重量%である。

【0043】

超臨界二酸化炭素の温度制御は、温度制御装置58により行う。処理室14の内部圧力が一定圧力以上になると、排圧弁52が開き、排出液分離装置54を経由して超臨界二酸化炭素と洗浄助剤とが系外に排出される。

このように、処理室14内に充填された超臨界二酸化炭素を適宜排出することにより、処理室14内の圧力、温度を一定に保つことが可能である。

洗浄助剤を添加した超臨界二酸化炭素に被洗浄体Wを所定時間、例えば10分間浸漬して、重金属汚染物を除去する。次いで、洗浄助剤を添加した超臨界二酸化炭素に被洗浄体Wを浸漬させたまま、開閉弁40を閉止して洗浄助剤の供給を停止し、リンス液として超臨界二酸化炭素のみを処理室14に供給して、洗浄助剤濃度を徐々に薄めつつ洗浄助剤を排出する。二酸化炭素と洗浄助剤の混合廃液は、排出液分離装置54で分離され、必要に応じて回収再生される。

【0044】

その後、処理室14を降圧して、二酸化炭素を排出し、冷却すると、被洗浄体Wは、気体の二酸化炭素に満たされ、乾燥する。超臨界乾燥では、例えば超臨界流体として二酸化炭素を用いた場合には、例えば、温度を40℃、圧力を10MPaに保持して洗浄した後、温度を31.1℃以上に保持しつつ、圧力を大気圧まで減圧する。その後、温度を31.1℃以上から室温、例えば、20℃に下げる。

これによって、処理室14内の被洗浄体Wは乾燥状態になる。このように、超臨界乾燥を経ることで、多孔質低誘電率膜の孔のような微細構造を有する被洗浄体Wの微細構造を破壊することなく、乾燥させることが可能とな

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る。
以上の工程を経ることにより、被洗浄体Wに付着している重金属汚染物を除去し、清浄な被洗浄体Wを得ることができる。

【0045】

実験例1

実験例1として洗浄前にCu原子が 10^{13} atom/cm² 程度付着していた図6(c)に示す積層構造を有するウエハを本実施形態例の方法により洗浄／乾燥処理したところ、図2に示すように、ウエハのCu原子の付着量を 10^{10} atom/cm² 程度に低減することができ、十分な重金属汚染除去を達成することができた。

比較例として、洗浄助剤を添加せず超臨界二酸化炭素のみを処理流体として実験例1と同じウエハを洗浄／乾燥処理したところ、ウエハのCu原子の付着量は 10^{12} atom/cm² 程度であって、Cu原子の付着量は洗浄前と余り変化はなかった。

【0046】

実験例2

また、図6(a)に示す、配線層成膜前の多孔質低誘電率膜を実施形態例1の洗浄方法によって洗浄したときの多孔質低誘電率膜の洗浄前の構造(組成)と、洗浄後で配線層成膜前の構造(組成)とを赤外分光分析を用いて調べ、洗浄前後の組成変化を図3に示した。

図3は横に赤外吸収スペクトルの波数(cm^{-1})を縦軸に吸光度(任意目盛)を取り、上段に洗浄前の赤外吸収スペクトルの波数(cm^{-1})と吸光度との関係を示すグラフ、下段に洗浄後の赤外吸収スペクトルの波数(cm^{-1})と吸光度との関係を示すグラフを示している。尚、洗浄前後の吸光度は同じであるが、ピーク波数の位置を明確に示すために、上下に分離して表示している。

【0047】

図3から判るように、洗浄前後で、多孔質低誘電率膜を構成しているSi-O、Si-H、Si-OH、Si-CH₃、C-Hなどの結合に変化は見られなかった。従って、洗浄前後で組成変化が生じていない、つまり洗浄前後で低誘電率膜の構造に変化はないので、孔が潰れて誘電率が変化するようなことも生じていないと判断できる。

実験例1及び2から判るように、超臨界二酸化炭素には気液界面が生成していないので、従来のように、洗浄及び乾燥に際し、多孔質低誘電率膜が気液界面を通過して多孔質の孔が潰れるようなことなく、重金属汚染物を除去し、乾燥させることができることが確認できた。

【0048】

尚、洗浄助剤を超臨界二酸化炭素に注入する前に、開弁弁46を開放し、極性溶剤供給手段44により極性有機溶剤供給源24から供給ライン42及び三方弁34を経

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由して超臨界流体に注入しておく、一層、洗浄助剤の溶解度を高めることができる。極性有機溶剤の添加比率は、1%以上20%以下である。

【0049】

金属膜の研磨方法として、化学的機械研磨(Chemical Mechanical Polishing: CMP)を例にして説明したが、研磨方法としてはCMPだけに限られるものではない。例えば電解研磨(Electro Chemical Polishing: ECP)などで発生する重金属汚染も同様に、本発明の洗浄方法により、多孔質低誘電率膜の構造を変化させることなく、除去することができる。

【0050】

本実施形態例の方法では、被洗浄体として、LSIの製造工程で形成する、多孔質低誘電率膜を用いた配線構造を備えたウエハを例にしているが、LSIの製造工程で形成するその他の多くの微小構造体にも同様に適用可能である。

また、エアーブリッジ構造からなる可動部を有するマイクロマシンであって、重金属汚染されたものを被洗浄体として本実施形態例の方法を適用したところ、洗浄後に、エアーブリッジ表面が従来のように侵食されることなく、また、エアーブリッジの基板への貼り付きもなく重金属汚染物を除去できることを確認した。

【0051】

実施形態例2

実施形態例1では、多孔質低誘電率膜に埋め込み配線を設けたウエハであって重金属汚染された被洗浄体を洗浄／乾燥処理しているが、本発明方法はこれら以外の被洗浄体にも適用できる。

本実施形態例は、大規模集積回路に設けた図4に示す高アスペクト比のパターンを有する脆い構造の電極構造の洗浄に、第1及び第2の発明方法に係る洗浄方法を適用した実施形態例である。図4(a)から(c)は、それぞれ、電極構造を形成する際の各工程の断面図である。本実施形態例では、先ず、図4(a)に示すように、Si基板62上に第1の層64として薄い絶縁膜を形成した後、順次、第2の層(絶縁膜)66、第3の層(金属膜)68、及び第4の層(絶縁膜)70を成膜して、積層構造を形成する。

レジスト膜を第4の層70上に塗布し、フォトリソグラフィ処理を行ってレジストマスク72を形成する。

続いて、レジストマスク72上からドライエッチング法により第4の層70、第3の層68、及び第2の層64をエッチングして、図4(b)に示すように、第3の層(金属膜)68からなる微細なパターンの電極構造74をSi基板62の第1の層64上に形成する。

【0052】

ところで、図4(b)に示すように、第2の層64と第3の層68の側壁にはエッチング残渣や重金属汚染物が

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付着しているのを、除去する必要がある。

レジスト除去工程では、レジスト材のような有機成分の残渣は除去できるが、重金属汚染物を除去することはできない。そこで、レジスト除去工程とは別に、重金属汚染物を洗浄、除去することが必要になるが、通常の洗浄液による洗浄では、パターンのアスペクト比が大きく、電極構造 7 4 のパターンが倒壊する。

そこで、実施形態例 1 と同様にして、洗浄／乾燥装置 1 0 を使用し、超臨界流体、例えば超臨界二酸化炭素に洗浄助剤として有機酸またはキレート剤を添加して、電極構造 7 4 を洗浄処理することにより、微細なパターンを倒壊させることなく、図 4 (c) に示すように、重金属汚染物を除去した微細な電極構造 7 4 を形成することができる。

【0053】

【発明の効果】

第 1 の発明方法によれば、洗浄助剤として有機酸又はキレート剤を所定添加率で添加した超臨界流体を洗浄液として使用し、洗浄助剤を添加した超臨界流体に被洗浄体を接触させて洗浄する洗浄工程を有することにより、多孔質低誘電率膜の孔等の被洗浄体の微細構造を損傷させることなく、有機酸またはキレート剤の金属捕捉作用により、重金属汚染物を確実に洗浄、除去し、被洗浄体を乾燥させることができる。

また、マイクロマシンのエアブリッジやカンチレバーのような梁形状の微小構造体からなる被洗浄体の洗浄に第 1 及び第 2 の発明方法を適用した場合にも、微小構造体に損傷を与えることなく、重金属汚染物を洗浄、除去することができる。

第 2 の発明方法によれば、1 槽式の洗浄／乾燥装置により、重金属汚染物で汚染された被洗浄体の洗浄、浄化、及び乾燥を一括処理することができる。

また、第 1 及び第 2 の発明方法では、エッチング作用或いは酸化作用を有する化学物質を添加する必要がないので、例えば多孔質低誘電率膜に形成された埋め込み配線が侵食されて、配線抵抗が上昇する等の問題が生じない。

【図面の簡単な説明】

【図 1】実施形態例 1 の方法を実施する際に使用する洗浄／乾燥装置の構成を示すフローシートである。

【図 2】図 2 は、実験例 1 及び比較例での被洗浄体の洗浄前後の重金属汚染物（パーティクル）の数を計数した

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結果を示す棒グラフである。

【図 3】横に赤外吸収スペクトルの波数 (cm^{-1}) を縦軸に吸光度（任意目盛）を取り、上段及び下段に、それぞれ、洗浄前及び洗浄後の赤外吸収スペクトルの波数 (cm^{-1}) と吸光度との関係を示すグラフを示している。

【図 4】図 4 (a) から (c) は、それぞれ、電極構造を形成する際の各工程の断面図である。

【図 5】図 5 (a) から (c) は、それぞれ、多孔質低誘電率膜を使い、シングルダマシンプロセスにより金属配線及び金属プラグを形成する際の各工程を説明する断面図である。

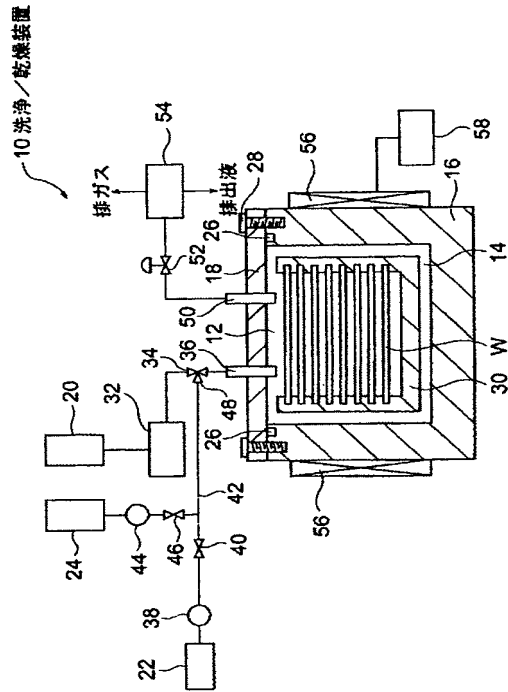
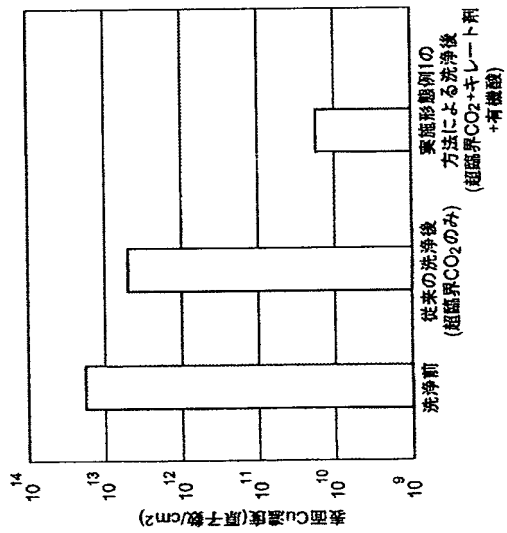
【図 6】図 6 (a) から (c) は、それぞれ、それぞれ、多孔質低誘電率膜を使い、デュアルダマシンプロセスにより金属配線及び金属プラグを説明する際の各工程を説明する断面図である。

【符号の説明】

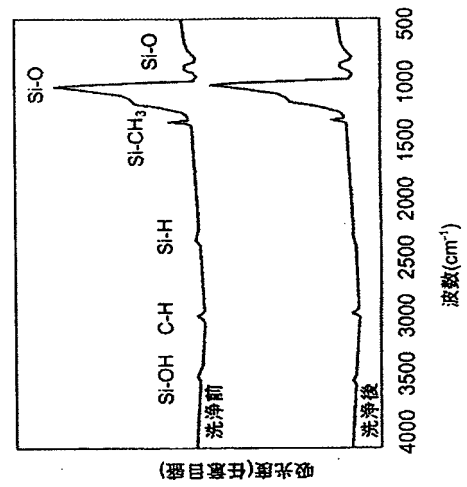
1 0 ……洗浄／乾燥装置、1 2 ……開口部、1 4 ……処理室、1 6 ……チャンバ、1 8 ……蓋、2 0 ……流体供給源、2 2 ……洗浄助剤供給源、2 4 ……極性溶剤供給源、2 6 ……リング、2 8 ……締め付け具、3 0 ……被洗浄体保持カセット、3 2 ……圧力・温度制御手段、3 4 ……三方弁、3 6 ……流体供給ポート、3 8 ……洗浄助剤供給手段、4 0 ……開閉弁、4 2 ……供給ライン、4 4 ……極性溶剤供給手段、4 6 ……開閉弁、4 8 ……供給口、5 0 ……流体排出ポート、5 2 ……排圧弁、5 4 ……排出液分離装置、5 6 ……加熱手段、5 8 ……温度制御装置、6 2 ……Si 基板、6 4 ……第 1 の層（薄い絶縁膜）、6 6 ……第 2 の層（絶縁膜）、6 8 ……第 3 の層（金属膜）、7 0 ……第 4 の層（絶縁膜）、7 2 ……レジストマスク、7 4 ……電極構造、7 6 ……下地膜、7 8 ……エッチングマスク層、8 0 ……多孔質低誘電率膜、8 2 ……コンタクトホール、8 4 ……配線溝、8 6 ……反応防止層、8 8 ……金属膜、9 0 ……金属プラグ、9 2 ……埋め込み配線、9 3 ……重金属汚染物、9 4 ……下地膜、9 6 ……第 1 多孔質低誘電率膜、9 8 ……第 1 エッチングマスク層、1 0 0 ……第 2 多孔質低誘電率膜、1 0 2 ……第 2 エッチングマスク層、1 0 4、1 0 6 ……コンタクトホール、1 0 8 ……配線溝、1 1 0 ……反応防止層、1 1 2 ……金属膜、1 1 4、1 1 6 ……金属プラグ、1 1 8 ……埋め込み配線、1 2 0 ……重金属汚染物。

【図 1】

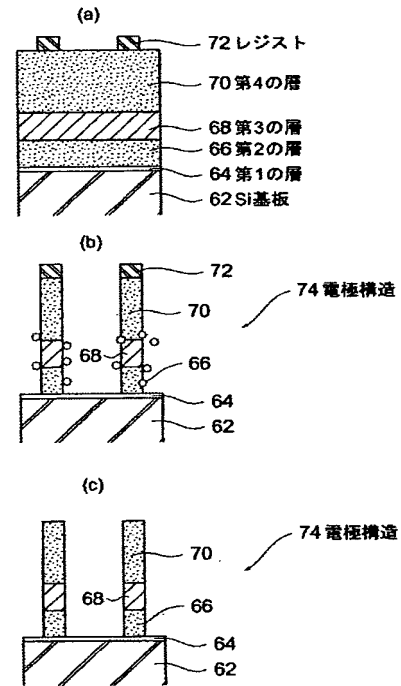
【図2】



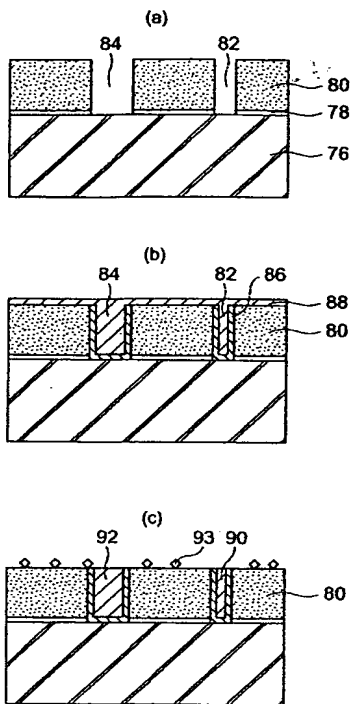
【図3】



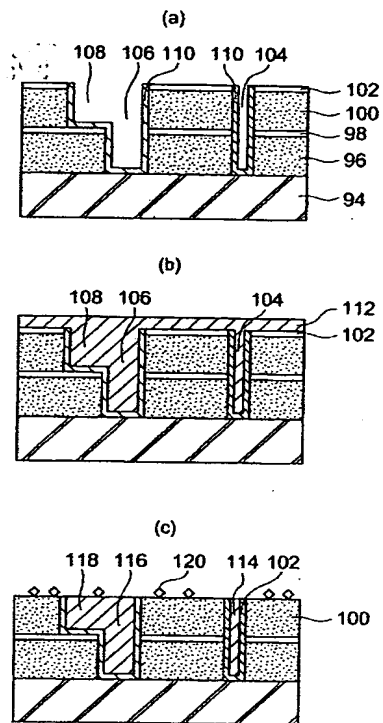
【図4】



【図5】



【図6】



フロントページの続き

(51) Int. Cl.⁷

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テーマコード (参考)

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